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Yields and properties of char produced by slow pyrolysis of lignocellulosic biomasses

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Abstract

Restoration of soils contaminated by potentially toxic elements (PTEs) can be carried out through phytoremediation technique. Biomasses to be used in the phytoremediation process are generally selected to match agronomic parameters and heavy metals uptake ability. The environmental sustainability of the phytoremediation could be supported in combination with further process useful for the disposal of the contaminated biomasses. The safe disposal of contaminated biomasses in landfills remains an unresolved problem. To implement phytoremediation properly, a plan for the disposal or valorization of the contaminated plant material after harvesting is required.

Pyrolysis can represent an environmentally sustainable strategy capable to reduce the volume and weight of contaminated matter with respect to the original biomass; concentrate the potentially toxic elements (PTEs) in the solid product and produce a vapour phase heavy metal free energy carrier. The stability of PTEs and the physico-chemical properties of the produced chars are relevant to assess if the contaminated char could be converted into a valuable resource. Such issues are currently largely unexplored in literature.

Mainly the char characteristics depend on the feedstock composition and pyrolysis conditions, a proper selection, of the biomasses suitability for the phytoremediation, could be greatly effective if the knowledge of the possible properties of the residual char from pyrolysis is available to identify possible valorization routes.

In this Ph.D. thesis, a comparative analysis of the yields and phisco-chemical characteristics of char obtained from slow pyrolysis (at constant heating rate, HR_{sp} = 4 K/min, and pressure, P = 5*105 Pa) of five uncontaminated biomasses (Populus nigra, Salix alba, Fraxinus oxyphylla, Eucalyptus occidentalis and Arundo donax) is carried out under steam atmosphere to better develop char porosity. Moreover, the dependence of the properties of solid residue on the process final temperature is studied for E. occidentalis in the temperature range of 688–967 K. The results demonstrate that, among the studied biomasses, chars from P. nigra and E. occidentalis have to be preferred for applications regulated by surface phenomena given their highest surface area (270–300 m^2/g), whereas char from E. occidentalis is the best choice when the goal is to maximize energy recovery.

On the basis of the experimental results from the two sets of pyrolysis tests, Eucalyptus occidentalis, Populus nigra and Arundo donax are selected for phytoremediation test. Arundo donax is included within the phytoremediation test, due to its spontaneous growth in contaminated soils and easily harvesting.

The results of the feedstock characterization have shown that no heavy metals content is accumulated in Eucalyptus occidentalis, whereas Pb, Cd, Zn, Cu are stabilized in different plant parts of Populus nigra and Arundo donax.
The effect of the variable feedstock (branches and leaves for Populus nigra; rhizomes and culms for Arundo donax).and of the temperature, in the range 613-873 K, are studied for the investigation of the fate of Pb, Cd, Cu and Zn during pyrolysis.
The results obtained in this work of thesis show that when a slow pyrolysis process in has to be used for the treatment of the heavy metals contaminated biomasses the type of pollutants should be assessed. In presence of Cd it is necessary to operate at low temperature conditions (less than 553 K) to avoid the release of Cd into the combustible gaseous phase. However, under these conditions, the char characteristics do not allow to use it in processes that involve solid-fluid interface phenomena (e. g. adsorbing material, catalysis, synthesis of composite materials). The pyrolytic treatment represents only a safe biomass disposal process that combines the reduction of the volume of contaminated solid, with an increase in its recalcitranza, and a reduction of the mobility of heavy metal, that remain confined in the char in a more stable form.
If the biomasses are only contaminated with one or more metals between Pb, Cu and Zn, it is possible to conduct a pyrolytic treatment at higher temperatures, thus obtaining a solid residue of interest in all applications that require a high specific surface, with retained metals present in more stable form hardly and bioavailable, except for specific cases as was the case of Arundo rhizomes.

Contents

Introduction

1. Biomass as renewable source of energy and matter

The discussions of the international energy community revolve around some deeply interconnected focal points summarised in the so-called "Energy trilemma", energy security, energy equity and environmental sustainability. Geopolitical and environmental needs are currently pushing towards a revolution of the world's energy systems in two prevailing directions. The first is aimed at changing the supply structure both in terms of sources (decarbonisation of the energy system) and in terms of production models (transition to the decentralized small-scale production model); the second is aimed at containing the increase in energy demand by improving the efficiency of production, distribution and use of energy.
In this context, attention to renewable energy sources is born and developed since they are suited to respond to the different needs of the "Energy trilemma": Increasing the share of renewable energy use would reduce the high dependence on fossil imports in many countries.
Renewables are particularly suited both for the availability of resources and for the scale of the plant in a distributed energy generation system more flexible to the fast variations of the energy demand.
Current systems for capturing CO_2 from fossil fuel plants are still very expensive and represent a serious penalty of the plant's energy efficiency.
Among the renewable energy sources, biomass produced via cropping systems has a huge technical potential if high yielding energy crops are produced. However, this category raises a number of sustainability issues, such as competition for land with food and feed production, water availability and quality, and soil quality. Also, if new lands are used for energy crops, issues such as biodiversity and net greenhouse gas emissions from land use change becomes important. On the contrary, the residual biomasses are particularly interesting because of their adaptability to the concept of "circular economy", in which the objective is to exploit and transform the by-products of other production processes before them becoming a waste.
Their importance is greater because they can be exploited not only as a source of energy but also as a source of new materials. Indeed, over the last few decades have grown the interest in creating combined biobased energy and materials supply chains. One major challenge with biomass conversion processes is their economical sustainability related to the seasonal availability of feedstock, costs of transportation to central processing units and requirements of process heating. Their importance is greater because they can be exploited not only as a source of energy but also as a source of new materials. Indeed, over the last few decades have grown the interest in creating

combined biobased energy and materials supply chains. One major challenge with biomass conversion processes is their economical sustainability related to the seasonal availability of feedstock, costs of transportation to central processing units and requirements of process heating. It should be noted that when the cost is very expensive in terms of use of the use mechanically for the removal and transport of the soil and plants, the installation of a plant for the green-energy-biomass in situ could be the solution. In the study of Ghaffariyan (2017), provides a state-of-the art overview of forest biomass harvesting technologies and supply chains for several countries. In the work is reported that it should be taken into account that to solve operational problems of indeed any in-stand biomass operations needs to be optimized considering the biomass and harvesting method, the efficient technologies and the fleet design and trucks productivity and availability.
Truck transportation remains one of the largest costs of the biomass supply chain.
In this context, the proposed process must be evaluated with a distributed energy generation strategy in mind, in which the biomass, representing a residue/waste of processing plants, is processed in the proximity of the production sites. In addition, energetic sustainability of the char production has to be evaluated on the basis of vapour phase fuel yields and characteristics. Moreover, the prospective applications of the chars could improve the eco-sustainability of the process.
An alternative to the co-combustion of biomass and coal in large-scale CHP plants is represented by the creation of a local supply chain in which the residual biomass coming from another transformation process is processed on site in an integrated system for the combined recovery of energy and material that is flexible with respect to the products (energy or material) according to the energy demand of the local distribution network in which the system is located.
Residual biomasses can derive from different sources:

- Biomasses grown ad hoc on marginal land unsuitable for "food" production, such as, for example, soils subjected to severe erosion, salinized areas with low agronomic fertility and agricultural areas polluted by incorrect land use.
- Residues from agro-industry and agricultural activity.
- Biomass residues from biochemical treatments for the production of liquid and gaseous biofuels.

Focusing the attention to the first group it is worth to be noted that in the last years a great interest has grown to a new practice for the restoration of polluted areas through the use of specific plants, the phytoremediation. In this context exploitation of the plants grown on these polluted areas is strictly dependent on the fate of the pollutants during the transformation process.

1.1 Plants from phytoremediation process

Government, industry, and the public opinion now recognize the potential dangers that complex chemical mixtures pose to human health and for the environment, especially for the surface and underground water. The most important aim is to decrease pollutant levels and stop the spread of the contamination in the soil, preventing any damage to the aquifers. The European Environment Agency (EEA) has identified heavy metals (Pb, Cd, Zn, Cu) and mineral oils as the main pollutants of the soil, namely Potentially Elemental Toxits (PETs), as well as metalloid elements and polycyclic aromatic hydrocarbons (PAHs) and in harder conditions the dioxins.

Although, the global map of the contaminants is difficult to define (EEA - 2014/2016), several definitions are used to describe the contaminated land or "brownfield lands" (Kovacs et al. 2016). The term brownfield land most commonly refers to disused, industrial or commercial sites that are difficult to redevelop due to existing pollution (NICOLE Brownfield Working Group, 2011). The issue that concerns the restoration of the brownfield lands is difficult to face in relation to the applicability, advantages, limitations and concerns, site-specific parameters, and costs of each alternative remediation. The contaminants and site characteristics determine which one of the many remediation techniques available are used in any given situation, each one having their advantages and disadvantages (Khan et al., 2004). Several physical, chemical and biological technologies are available in relation to the kind of pollutants. The important key factor is the feasibility, velocity and economics. Where the requirements for in-situ processes are met, phytoremediation is one of the most attractive techniques. This process is a promising inexpensive and aesthetically acceptable in situ clean-up technology that exploits the natural ability of plants to remove contaminants from the environment or to make toxic compounds harmless (Polle et al., 2013).

Phytoremediation has been applied to a number of contaminants in small-scale field and laboratory studies (Khan et al., 2004; Özkan et al., 2015).

This process is based on the ability of the lignocellulosic and herbaceous plants, called “hyper-accumulator plants” to absorb, transfer and stabilize contaminants by roots followed by translocation and accumulation in areal parts (Yao et al., 2012).

Different five basic mechanisms are involved in the phyremediation:

- phytoextraction
- phytotransformation
- rhizodegradation,
- phytostimulation
- phytostabilization

Phytoextraction utilizes the ability of plants to absorb inorganic pollutants and translocate them to different organs. The plants are able to accumulate heavy metals, such as lead, cadmium and zinc, thus decreasing the concentration of the contaminants in the soil and rehabilitating the site (Yaapar and Binti, 2008).
In non-accumulative plants, the accumulation of micronutrient metals does not exceed the metabolic needs of the plant (<10ppm). On the contrary, the so-called hyperaccumulator plants are conventionally defined as species able to accumulate metals at levels 100 times higher than those typically measured in non hyperaccumulator plants; they can, therefore, absorb up to about 10 ppm of Hg, 100 ppm of Cd, 1000 ppm of Co, Cr, Cu, and Pb and 10000 ppm of Ni and Zn (Revees et al, 1999).
The polluting compounds and elements are transported into the roots and above ground parts of the plants, both of which can be easily harvested.
Important observations related to the performance of phytoremediation technology are:

- Remediation is accomplished with minimal environmental disturbance, in which is not necessary to feed the process with external energy, but it is a passive, solar energy-driven technology for the growing of the plants.
- It can be used on a large range of contaminants when the concentrations are low in the soil, and it is cost-effective especially for large sites. The extensive contaminated areas are also aesthetically regenerated with a low environmental impact.
- The topsoil is left in a usable condition and may could be used even in agriculture after the restoration. The soil can remain in site after the removal of the contaminant rather than being disposed of or isolated.
- Organic pollutants may be converted to CO_2 and H_2O instead of transferring toxicity.
- Remediation usually requires more than one growing season, in relation to the species adopted, but the limiting factor is the time required to successfully clean the contaminated site.

The environmental sustainability of the phytoremediation could be supported in combination with further process useful for the disposal of the contaminated biomasses. The safe disposal of contaminated biomasses in landfills remains an unresolved problem. To implement phytoremediation properly, a plan for the safe disposal of the contaminated plant material after harvesting is required. This work of thesis is framed in the European LIFE ECOREMED project that is now implementing an eco-compatible protocol for soil restoration through phytoremediation in Litorale Domitio - Agro Aversano NIPS (South Italy, Campania region). The aim of the project is to define the procedures for soil

restoration and also for the safe disposal of the biomass deriving from the phytoremediation.
Sas-Nowosielska et al. (2004) evaluated different disposal options: composting, compaction, direct disposal, leaching, torrefaction, pyrolysis, and incineration (combustion and gasification). Composting and compaction have been proposed as post-processing treatments, as both of them are capable of greatly reducing the volume of the harvested biomass (Ghosh and Singh, 2005). Nevertheless, the high solubility of heavy metals in the leachate from these processes warrants additional treatments to ensure their appropriate collection and disposal. Reviewing the literature, it can be stated, that the gasification and combustion of contaminated biomass is not an ordinary biomass firing process. The particles in the flue gas contain metal compounds, thus making the application of an efficient air cleaning system mandatory.
A more appealing approach consists in utilizing the contaminated plants as feedstock in a bio-based energy and/or material supply chain. Pyrolysis can be explored as a possible thermal treatment capable of producing, in the absence of molecular oxygen, a solid residue (char) suitable for application in several fields (as a fertilizer, activated carbon, etc.) and a liquid (bio-oil) and gaseous products that can be exploited for energy applications.
Char valorization is a key point for the feasibility of the whole phytoremediation process (Kuppens et al., 2015). Review of the literature suggests many possibilities for valorizing char potential for diverse applications such as:
- fuel in traditional and advanced power generation facilities (Kambo and Dutta, 2015; Qian et al., 2015);
- fertilizer and carbon sink (Lehmann and Joseph, 2009; Kambo and Dutta, 2015; Qian et al., 2015; Amin et al., 2016);
- contaminant adsorbent in wastewater and soil (Downie et al., 2009; Keiluweit et al., 2010; Kambo and Dutta, 2015; Beesley et al., 2011; Tan et al., 2015; Qian et al., 2015);
- adsorbent or catalyst for gas cleaning (Shen, 2015; Qian et al., 2015);
- catalyst for syngas conversion to liquid hydrocarbons and biodiesel production (Qian et al., 2015);
- raw material for supercapacitors (Qian et al., 2015) and
- filler in wood and polymer composites (Das et al., 2015b).

2. Aim of the thesis

This experimental thesis was carried out at laboratory of "Institute for Research on Combustion" (IRC). The PhD project is the one of the different sections of the European "LIFE-Ecoremed" project, financially supported by European Community in which have been involved different Departments of Univeristy of Naples "Federico II" and research centers of Campania Region (Italy). The main goal of the project was implementing an eco-compatible protocol for soil restoration through phytoremediation in Litorale Domitio - Agro Aversano NIPS (South Italy, Campania region).
Biomasses to be used in the phytoremediation process were generally selected to match agronomic parameters, such as absence from the trophic chain, high biomass production, and ability to uptake heavy metals, high growing rate, high adaptability to the climatic conditions, and high resistance to biotic and abiotic stresses. Based on these criteria, the ECOREMED project selected five biomasses, namely Populus nigra, Salix alba, Fraxinus oxyphylla, Eucalyptus occidentalis and Arundo donax. However, the safe disposal and the valorization of the contaminated biomass is a key point for the feasibility of the whole phytoremediation process. In this work of thesis pyrolysis is studied as possible thermochemical treatment of the contaminated biomasses with the aim to:

- concentrate heavy metals in the solid product (char), thus reducing the volume and weight of contaminated matter (Stals et al., 2010a, b; Lievens et al., 2008a,b).
- produce a combustible gaseous product containing no or limited amounts of heavy metals (Stals et al., 2010a, b; Lievens et al., 2008b) that can be used to assist energetically the pyrolysis process.
- tailor the characteristics of the char (William and Besler, 1996) thus making it suitable for use in other applications.

The work is structured in two parts, in the first part the structural properties of not contaminated biomasses as function of the thermal conditions are assessed, whereas in the second part the fate of the heavy metals during the pyrolysis of contaminated biomasses conducted in the same conditions has been studied.
As for the first part, the data from the presented literature survey are somewhat useful for the assessment of possible char applications. However, the species tested in different studies were grown on different soils using different agronomic procedures. Moreover, they were harvested during different periods of their growth, and the pyrolysis operating conditions, even though in the range of slow pyrolysis, differed greatly from one study to another, thus making it extremely hard to compare the char characteristics. Moreover, it is worth to be noted that slow pyrolysis experiments are typically carried out in an inert

environment (nitrogen or helium), whereas, as emerged from the literature review, steam as compared with nitrogen and carbon dioxide is more interesting given its influence on the liquid quality and physical properties of char. As the effect of steam on char properties presumably varies with the considered feedstock, the present work attempts to meet the need of a comparative analysis of steam assisted pyrolysis of the five biomasses of interest for the project grown on the same soil by assessing the yields and chemical and structural characteristics of the corresponding chars produced under comparable slow pyrolysis conditions.

Two sets of slow steam assisted pyrolysis experiments were carried out at constant heating rate, HR_{sp} = 4 K/min, and pressure, P = $5*10^5$ Pa. In the first set, all the selected biomasses were pyrolyzed up to the final temperature, T_f = 873 K; whereas, in the second set, pyrolysis of Eucalyptus occidentalis was carried out in the temperature range 688-973 K, namely 688, 794, 873, and 967 K. For each pyrolysis test set the products yields were determinate and the products characterized. The evaluation of the char properties (Proximate, Elemental, ICP/MS, BET analysis, isotherm pore size distribution, pH, HHV), were performed in order to identify its best properties and possible correlations with the chemical-physical nature of the feedstock and with the thermal effect of the pyrolysis.

On the basis of the results obtained from the first experimental pyrolysis campagne, Eucalpytus, Populus nigra and Arundo donax were chosen for phytoremediation test. The results of the feedstock characterization have showed that no heavy metals were accumulated in Eucalyptus occidentalis, whereas opposed resuts were obtained for Populus nigra and Arundo donax, in which Pb, Cd, Zn, Cu were stabilized in different parts of the plant.

In the second part of the thesis Populus nigra and Arundo donax were studied for the investigation of the distribution of Pb, Cd, Cu and Zn in the pyrolysis products and the influence of the plant parts was considered. Also for the contaminated biomasses two pyrolysis sets were conducted under the same conditions of the first part, except for the final temperature. In the first set, Populus nigra branches and leaves were pyrolysed in the temperature range 613-873 K, whereas in the second set Arundo donax, rhizomes and culms were investigated in the temperature range 703-873 K. The distribution and the stability of the heavy metals in the produced chars have been evaluated and the physico-chemical properties have been assessed.

3. Context of the work

In order to identify pyrolysis in the more general framework of the thermochemical conversion technologies for the sustainable integration and valorization of biomass a brief presentation of the main thermochemical processes and of pyrolysis in general is given. Then a literature survey on the slow pyrolysis for the production of char is presented. Finally, the main achievements on the fate of heavy metals during biomass pyrolysis are discussed.

3.1 Pyrolysis

The main thermochemical processes include gasification, pyrolysis, and torrefaction. Gasification, pyrolysis, and torrefaction are all performed in absence of oxygen or with significantly less oxygen than what is required for complete combustion. The operating conditions and the yield and distribution of products varies between these three processes. Gasification, pyrolysis, and torrefaction cannot be defined as completely separated processes because, for instance, pyrolysis can be considered as an incomplete gasification process and torrefaction an initial stage of gasification or pyrolysis. Combustion is naturally also a thermochemical conversion process, however, with heat and power as the main output. In Figure 2.1, the major differences between combustion, gasification, pyrolysis, and torrefaction are illustrated in terms of operating conditions and products.

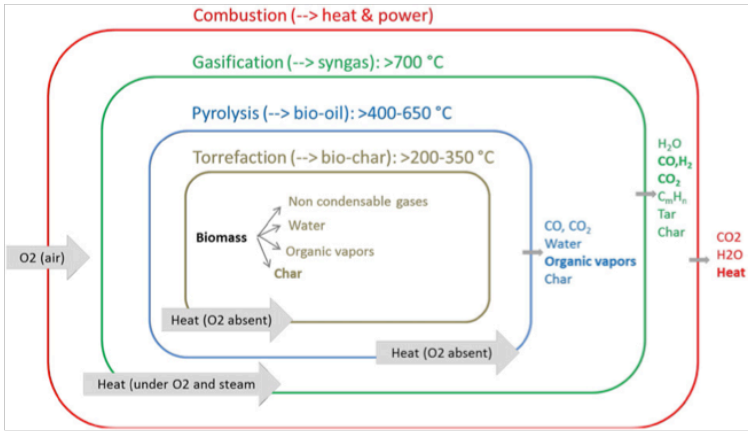

Figure 2.1: General overview of combustion, gasification, pyrolysis, and torrefaction (adapted from Matsakas L. et al., 2017).

Pyrolysis is the process that allows the combined production of condensable vapours and gases (CO, CO_2, CH_4, H_2) with a solid residue rich in carbon, the char, whose characteristics and yields depend on the operating conditions (Bridgwater et al., 1999).
Depending on the operating conditions, the pyrolysis is defined as slow, intermediate or fast. For high temperatures and long residence times, biomass conversion to gaseous phase is pushed; moderate temperatures and short residence times are ideal for the production of liquids, and finally, for low process temperatures and long residence times, the production of the solid product is favoured.

	Heating rate *°C/s*	*Temperature* *°C*	*Residence time*
Slow	0.01-2	300-700	min-h
Intermediate	0.01-20	<650	min
Fast	100-1000	400-600	sec

Table 2.1: Classification of thermochemical treatments in an inert environment (Bridgwater, 1999; Acharya, 2012)

Besides the above mentioned operating parameters, the yield of the products mainly depends on the chemical and physical variability of the different biomasses.
The primary operating parameters that influence a pyrolysis process are final temperature, sample heating rate, pressure, feedstock properties and flow rate of the pyrolyzing agent (Di Blasi 2009; Rao et al., 1998). The flow rate is strictly linked to the residence time of the gaseous phase in the reaction environment (Di Blasi 2009).

3.2 Thermal conditions

Several data relevant the pyrolysis of different biomasses (hard and sweet wood) in different reactors configurations (fluidized beds, fixed beds, single parcel etc.) have been collected by Di Blasi (2009). The trend of char yields from pyrolysis of wood residues as a function of the temperature in the range 600-1000 K conducted in fixed bed reactors (slow pyrolysis conditions), and in fluidized bed reactors (fast pyrolysis conditions) is shown in Figure 2.2.
At higher temperature, the primary degradation of biomass leads to the formation of the condensable phase at the expense of char, while the formation of gas (CO, CO_2, CH_4) is limited. For T>753 K the condensable fraction undergoes to a process of secondary degradation with the release of gas (CO, CO_2, CH_4 and H_2) and the formation of light condensable. At higher

temperatures heavy, condensable and secondary char whose structure is much more compact than that of the primary char are formed. When secondary reactions are activated, the condensable yield reaches a maximum, while the gas yield increases significantly and the char yield decreases more slowly due to secondary char production. For all types of biomass, gas yields increase with the temperature.

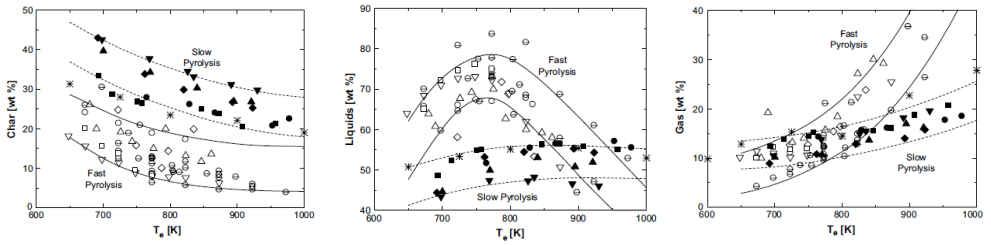

*Figure 2.2: Char, liquid and gas yield (%wt on dry basis) depending on the temperature of pyrolysis in fixed bed (slow pyrolysis conditions) (icon: filled and *), and fluid bed (fast pyrolysis conditions) (empty icon) (Di Blasi et al., 2009).*

The char produced by pyrolysis is a multiphase system, with carbon phase and a mineral phase associated with a liquid phase that occupies part of the porosity, thereby the determination of the content of fixed carbon, volatile fraction, and ashes is important. At low temperature (T< 523 K) the char resulting from the pyrolysis is the result of dehydration and depolymerization reactions of cellulose, so it consists mainly of oligosaccharides. Under these conditions, the condensable phase partially occludes the pores of the char. The condensed phase consists of both organic and inorganic compounds. At higher temperatures (523 K <T< 623 K) the char is mainly made up of amorphous carbon (organized in aromatic structures), for temperature between 573-873 K, the increase in the aromaticity of the structure corresponds to a decrease in the H/C and O/C ratio. The char produced in this temperature range is characterized by a high concentration of free radicals and it is therefore very reactive in oxidative environments. At higher temperatures, there is the growth of graphene layers and removal of O, H, N, and S. During pyrolysis, an increase in temperature corresponds to a reduction of the char yield, however, richer in fixed carbon due to the advancement of the aromatizing process. The ash yield is independent of the temperature, while the concentration increases with the temperature due to the decrease of the char yield (Lua et al., 2006). The effect of the temperature is considerable on the type and concentration of the char's superficial functional groups, which are important for the use of char. The activate sites determine the interaction of char with the chemical compounds present in the environment in which is possible to use it.

Inorganics species are present as hetero-atoms in the superficial functional groups of the carbonyl and carboxylic phase (OH, NH_2, OR, O (C=O)R, NO_2, carbonyl and carboxylic groups) or as mineral phase (K, Cl, N, Ca, Ca, Si, Mg, P, S, S, Mn, Fe in the form of salts, oxides, and hydroxides). The ions of K and Cl and N vaporize at low temperature. Also, the K concentration is reduced half between 473 and 900 K and, while at low temperature it is bioavailable as a nutrient, at a higher temperature it is incorporated in the silicate structure, which makes it less available (Yu et al., 2005). S is present partly in inorganic form as sulphate (40-50%) and partly as protein. 50% of S is already volatilized at 673 K as a result of organic decomposition. At higher temperature, the sulphates change from soluble to insoluble sulphates (Knudsen, 2004; Lang, 2005). Ca and Si and Mg, bounded with ionic and covalent bonds to organic molecules, are released at higher temperatures. Fe and Mn are present both in organic and inorganic form and are retained during pyrolysis. P is also retained during pyrolysis, but with the increasing of the temperature, the P transforms into a form that is not bioavailable.

The morphological characteristics of char are important for the use of char in many fields of application. There are two important parameters associated with the porosity of the char:

- specific surface area (BET surface), generally higher in the presence of a high microporosity ($d< 2$ nm);
- pore-volume, mainly determined by mesopores ($2<d<50$ nm) and macropores ($d> 50$ nm).

Macroporous volume mainly serve as access to micropores, indeed, diffusive limitations occur within the micropores that are no easily accessible. A high specific surface area guarantees a significant potential adsorbing ability of the char. However, the macropores also play an important role in the use of the char for soil amendment and fertilization, as an available volume for the micro-organisms growth and soil ventilation. The distribution of the pore diameter, specific surface area and volume are affected by the pyrolysis temperature and feedstock. Moreover, the pyrolysis temperature determines the distribution of organic molecules in the char and the evolution of the condensable present in the original porosity of the biomass. For $T< 874$ K the char has an amorphous structure with random crystalline graphene structures. During the pyrolysis, the crystalline areas and the organization of graphene planes grows. In addition, at increasing temperature, the devolatilization of the lighter condensables is favoured, with the corresponding increase of the total volume of pores and the specific pore surface (BET surface). At high temperature, the devolatilization causes thinning of the walls of the micropores, which can coalesce with the adjacent pores. This leads to an increase in the volume of pores, due to the reduction in micropores (reduction of the specific surface area). In addition, at high temperatures ($T> 900$ K) the condensed phase through re-polymerization,

occludes the pores reduces the total volume and specific surface area (Lua et al., 2004; Lua et al., 2006).
The specific surface area has a non-monotonous trend with the temperature and with the variable original biomass. Figure 2.3, panel "a" shows the trend of the specific surface area and volume of micropores in relation to the pyrolysis temperature, while Figure 2.3, panel "b" shows the trend with the temperature of the volume of mesopores and macropores and the average diameter of pores (Lua et al., 2003). The graphs are relative to the active carbon obtained from pistachio nut shells under slow pyrolysis conditions (HR=10°C/min)

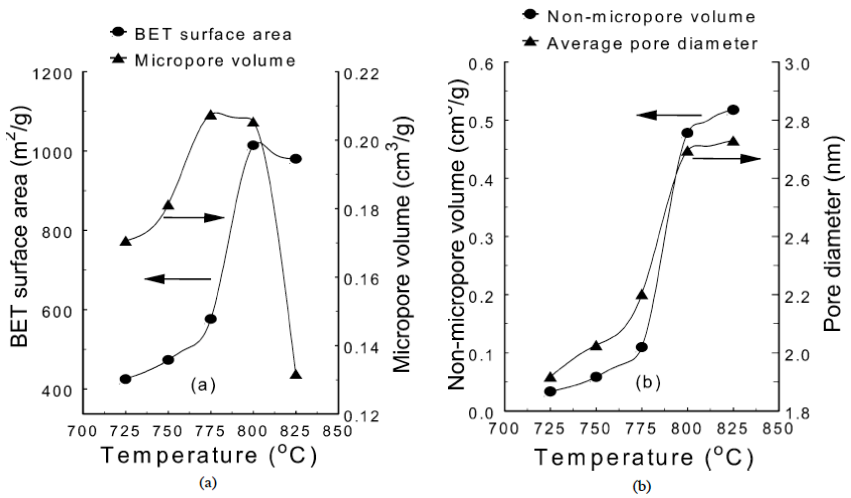

Figure 2.3: Specific surface area and volume of micropores (a), the volume of meso and macroporous and average diameter of pores (b) (Lua et al., 2003).

To sum up, it is possible to say that although char yield decreases with temperature a proximate analysis of bio-mass char produced at temperatures lower than 673 K shows that its volatile matter content is still high determining low values of specific surface area. An increase in carbonizing temperature has a positive effect on this property. Even if a higher final temperature produces greater gas yields and a more valuable syngas, the upper limit of temperature should be set at 973 K in order to avoid excessive consumption of char, particularly in presence of steam that determines the onset of the heterogeneous gasification reactions.
Also, the heating rates has an important effect during pyrolysis process. Slow pyrolysis conditions maximize char yield, at the expense of gas and liquid yields and optimize the chemical and physical properties of the char. In fact, low heating rates favor char formation, thus reducing biomass devolatilization and secondary degradation reactions that result from the sample experiencing a lower average temperature (Di Balsi 2009). Moreover, low heating rates (below

10 K/min) allow for a slow release of volatile compounds, which produces a final porosity that resembles the original porous structure of biomass. A high micropores fraction is fundamental for the attainment of a high specific surface area (Shen et al., 2010; Liu et al. 2008). Nonetheless, at too low heating rate, char is characterized by relatively high volatile content (Shen et al., 2010; Liu et al. 2008). The closer internal structure of char produced at low heating rates does not allow an easy escape of volatiles from the char particle, thus increasing the residence time of volatiles inside the char particle and favoring the polymerization of volatiles to form secondary char with pores occlusions (Souza eta al., 2009). These considerations suggest to explore heating rates greater than 5 K/min, while limiting the upper value to 40 K/min.

3.3 Pyrolysing agent

Pyrolysis experiments are typically carried out in an inert environment (nitrogen or helium) while an oxygenated gas (steam or carbon dioxide) is used as a pyrolyzing or gasifying agent, depending on the established thermal conditions. Previous studies involving with the production of char-based activated carbon show the positive effect of steam as compared with nitrogen and carbon dioxide on the liquid quality and physical properties of char (Sensoz et al., 2006). Using steam as a pyrolyzing agent, the yields of water-soluble liquid products increase at the expense of gaseous and solid products, given the ability of steam to perform a more efficient penetration of solid matter-enhancing desorption, distillation and removal of volatiles (Antal et al., 1996). On the contrary, during pyrolysis in the presence of nitrogen, higher char yields are obtained with lower porosity because of the deposition of carbonaceous material inside char pores (Antal et al., 1996). Moreover, steam seems to be the optimal diluting agent in nonconventional combustion systems that are operated in MILD conditions (Cavaliere and De Joannon, 2004). that are particularly suitable for low heating value fuels, such as the vapor phase produced by biomass steam pyrolysis.

Many studies investigate the chemical mechanisms occurring during steam gasification, but only few of them deal with the effect of steam in the pyrolysis stage (Orfao et al., 1999; Bonelli et al., 2001). As appeared from previous literature, in the steam gasification of biomass several reactions take place simultaneously the extent of which depends on the operating conditions. In the thermal conditions, typical of pyrolysis steam is only weakly involved in homogeneous and heterogeneous reactions. For temperature, higher than 800 K steam reforming and water-shift reactions involving primary tars take place resulting in a slight increase of H_2 and CO_2 yield. Heterogeneous reactions between steam and char occur mainly in presence of the ligninic component at

temperature higher than 873 K producing H_2 and CO_2, while the reactions between steam and cellulosic char are less relevant, though they start at lower temperature (higher than 773 K).
Moreover, the role of the pyrolyzing agent has been evaluated for its effect on char yield and morphology (Prasakeva et al., 2008). Therefore, to optimize the proposed process, an overall analysis of the effects of the abovementioned variables on both the yield of the products and their chemical and physical characteristics is required. On the basis of available data from the literature, steam has been chosen as the reacting atmosphere, and appropriate ranges of pressure (1–5 105 Pa), heating rate (5–40 K/min) and final temperature (673–973 K) have been selected.

3.4 Pressure

The effect of pressure on products yields distribution is not easily predictable because of the formation of tars that prevent the attainment of thermodynamic equilibrium of pyrolysis reactions (Di Blasi 2009). Limited and contradictory data are presented in the literature on the effect of pressure on pyrolysis product yields (Wall et al., 2001; Wang et al., 2001). However, previous studies on cellulose pyrolysis have demonstrated that an increase in pressure, generally linked to higher gas residence time in the reaction environment, generates higher char yields and produces lighter volatiles (Linder et al., 2003). Alternatively, pressures higher than $5x10^5$ Pa lead to the formation of fused intermediates on the char surface that favor the agglomeration of close char particles, thus reducing the specific surface area of the solid residue. This effect becomes more significant at heating conditions that are typical of fast pyrolysis (Linder et al. 2003, Sharma et al. 2004). Thus, a pressure range $2–5x10^5$ Pa is advisable if a good compromise between char yields and properties would be pursued.

3.5 Slow pyrolysis for the production of char

The survey of literature data dealing with the effect of thermal conditions of char yields and properties suggests that steam assisted slow pyrolysis conditions have to be preferred if a good compromise between char yields and good char characteristics would be achieved.

Knowledge of the physical properties and the chemical composition of biomass is of fundamental importance for interpreting the yields and qualitative characteristics of products obtained from pyrolysis.

The main constituents of biomass are cellulose, hemicellulose, and lignin. Cellulose is the structure of the plants, about 50 wt%, and is a linear polymer with a degree of polymerization higher than 10000 units of glucose; the hemicellulose, varying between 25-35 wt%, is a branched polymer but with a molecular weight and a degree of polymerization lower than cellulose. Among the hemicellulose, xylan is the most common. Finally, lignin, which accounts for 15-25 wt% of the biomass, and gives rigidity to the structure of the plant. The lignin is a complex branched polymer mainly made up of phenols, but in reality, the nature of lignin depends on the type of biomass. Woody biomass can be classified into softwood, generally belonging to conifers with a higher lignin content, and hardwood, angiosperm. Biomasses also contain less quantity of extractives (organic extracts such as triglycerides, tannins, phenols, alcohols) and inorganic minerals (ash). The content and nature of the ash depend on the type of plant and soil on which the biomass have grown.

These components vary considerably on dependence of the type and part of biomass, whether trunk, branches or leaves. Therefore, the study of the behaviour of the interactions between the different categories of wood, the different components, and the influence of the presence of extractive and inorganic materials, make it difficult to propose results of general validity.

The data from previous studies show that pyrolysis chars (Zanzi et al., 2002; Lee et al., 2013; Das et al., 2015c; Srinivasan et al., 2015) and activated carbons from one stage thermal treatments (Paraskeva et al., 2008; Savova et al., 2001) vary greatly in structure and chemistry due, in part, to the large degree of chemical heterogeneity of the feedstock. For example, Zanzi et al. (2002) found that, under steam-assisted slow pyrolysis conditions, the surface area of chars derived from different feedstocks ranged from 405 m^2/g to 940 m^2/g.

To the best of our knowledge, compared with fast pyrolysis studies, a limited number of recent papers are focused on the characterization of char produced by slow pyrolysis of the biomasses of interest for the ECOREMED project in which is involved this thesis.

Slow pyrolysis experiments of Populus have been conducted in the temperature range 673–873 K under heating rate conditions ranging from 2 to 20 C/min and holding times at the final temperature going from 0 to 4 h (Slopiecka et al., 2012; Marks et al., 2014; Zhang and You, 2013; Gu et al., 2013; Sun et al., 2014; Kloss et al., 2012; Veksha et al., 2014).

In these conditions, char yields slightly vary between 24.6 and 28.2 wt%. On the contrary, large variations are observed in the carbon content that increases with temperature from 67.3 wt% at 673 K (Kloss et al., 2012) to 81 wt % at 873

K (Sun et al., 2014). The specific surface area exhibits large variations in a very narrow temperature interval going from 823 K to 873 K. A high value of BET surface, 210 m^2/g, is obtained at 823 K in the pyrolysis conditions used from Zhang and You (2013). Cyganiuk et al. (2012) show that char from Populus wood is characterized by a narrow pore size distribution, which makes it suitable for use as a carbon molecular sieve.

Slow pyrolysis of Salix has been also investigated in the past literature (Kwapinski et al., 2010; Masek et al., 2013; Nowakowski et al., 2007; Nelissen et al., 2014). Char yields vary in the range 39.9–25 wt% for pyrolysis tests carried out in the temperature range 523–823 K under slow heating rate conditions and different holding times at the final temperature. BET surface is always very low (<2 m^2/g), although Cyganiuk et al. (2012) showed that, as for Populus, different species of Salix are able to produce a char with a narrow pore size distribution. Carbon content (70.7–84.8 wt%) is consistent with typical value for biomass chars in this temperature range.

Eucalyptus has been widely investigated (Guerrero et al., 2008; Abdullah et al., 2010; Kong et al., 2014; Sun et al., 2013). Slow pyrolysis experiments cover a wide temperature interval going from 573 to 1173 K under similar heating rates (5–10 C/min) and holding times ranging from 15 to 60 min. Char yields vary greatly from temperature lower than 673 K while small weight loss is observed between 673 and 1173 K. In this range char yield decreases from about 29 wt% to about 21 wt%. High BET surface is obtained by Guerrero et al. (2008), for Eucalyptus char heated at 10 C/min up 873–1073 K and hold for 1 h at a final temperature. It is worth to be noted that, differently from the chars obtained from Populus and Salix, in this case, adsorption porosimetry tests have been carried out using CO_2 as adsorbate that typically gives higher values of surface area with respect to N_2 given its ability to penetrate in the narrowest micropores within char structure. Chars obtained from Eucalyptus have a very high carbon content in all the explored temperature range being equal to about 80 wt% at 673 K (Abdullah et al., 2010) and to 90% at 1173 K (Guerrero et al., 2008), thus showing a high HHV even at low temperature (Martins et al., 2007; Abdullah et al., 2010).

Even though a limited number of literature studies is available for the characterization of char obtained from A. donax (Saikia et al., 2015; Zheng et al., 2013) a wide temperature range is explored going from 623 K to 900 K. Char yields decrease from about 45 wt% up to 33 wt% going from 623 to 923 K and the opposite trend is observed for carbon content.

A higher holding time reduces char yields at comparable pyrolysis temperature and heating rate. In the whole temperature range, the ash content is quite high (7.7–11.3 wt%) in agreement with the herbaceous nature of this biomass.

Low values of BET surface area are obtained, nevertheless, Zheng et al. (2013) found that slow pyrolysis of A. donax at temperatures lower than 673 K produces a char characterized by a high bioavailability of plant nutrients (N, P, and K).

Even though these data are somewhat useful for the assessment of possible char applications, the species tested in different studies were grown on different soils using different agronomic procedures. Moreover, they were harvested during different periods of their growth, and the pyrolysis operating conditions, even though in the range of slow pyrolysis, differed greatly from one study to another, thus making it extremely hard to compare the char characteristics. Moreover, it is worth to be noted that slow pyrolysis experiments are typically carried out in an inert environment (nitrogen or helium).

Previous studies involving with the production of char based activated carbon show the positive effect of steam as compared with nitrogen and carbon dioxide on the liquid quality and physical properties of char given the ability of steam to perform a more efficient penetration of solid matter enhancing desorption, distillation and removal of volatiles (Minkova et al., 2001).

As the effect of steam on char properties presumably varies with the considered feedstock, there is the need of a comparative analysis of steam assisted pyrolysis of the five biomasses of interest for the ECOREMED project by assessing the yields and chemical and structural characteristics of the corresponding chars produced under comparable slow pyrolysis conditions.

3.6 Fate of heavy metals during pyrolysis of biomass

Despite the advantages in energy and material recovery, thermochemical conversion of biomass remains a subject of debate because of the trace amounts of inorganic and organic pollutants (e.g., heavy metals, PTEs and dioxins) could be formed and emitted. The characteristics and distribution of these pollutants are highly dependent on the operating conditions and technologies used.

Pyrolysis represents, as mentioned above, an interesting process for the disposal of biomass contaminated by heavy metals used for phytoextraction processes. In this context, it is essential to monitor the distribution of these metals in pyrolysis products in order to concentrate them in the solid phase, thus

obtaining a gaseous and liquid phase that can be used as fuel. At our knowledge, there is only one study in literature (Stals et al., 2010a,b) on biomasses of interest for the LIFE ECOREMED project; therefore the research has been extended to other biomasses. However, the literature data are still scarce and are only produced in conditions of rapid pyrolysis for the production of liquid fuel.

Lievens et al. (2009) apply fast pyrolysis to two biomasses, birch and sunflower, sampled in two different areas heavily polluted by Cd, Zn and Pb in the province of Limburg (Belgium), while Stals et al. (2010a,b) apply flash pyrolysis willow grown in a pilot field in Balen (Belgium) polluted with the same heavy metals. In both studies, a fairly wide temperature range (623-873 K) was investigated

Zn doesn't devolatilize, at least in the temperature range considered during experiments (T<873); moreover, the nature of biomass does not seem to influence the devolatilization of Zn, since both birch and sunflower observe the same behaviour.

It is noted that, in the case of the process applied to birch, Zn compounds are only partially detected in the pyrolysis solid product; this is explained by considering the retention of Zn compounds by the quartz with which the reactor is built and by the sand used in the fluidized bed; the process of immobilising heavy metals by silicates in presence of oxygen or steam is reported in the literature: Jakob et al, (1996) describes the immobilisation of heavy metals in fly ash from municipal solid waste incineration plants at a temperature range of 950-1273K and in the presence of chlorides (6%) through alumina or silica compounds and heavy metals.

In flash pyrolysis conditions, the Zn devolatilize when the temperature rises and it is detected in gas phase, while in liquid phase it is practically absent.

This difference could be attributed to the nature of biomass, and thus to the different content and forms in which Zn is present in it, or to the higher heating rate in the case of flash pyrolysis compared to fast pyrolysis, which results in higher actual sample temperatures.

Cadmium is less stable than zinc, both under fast and flash conditions its recovery in solid phase decreases as the temperature increases.

In fast conditions, its content in liquid phase increases, while in flash conditions it is found both in liquid and gas phase. This difference could also be attributed in this case to the pyrolysis conditions and to the different forms in which Cd is present in the original biomass.

The char from the fast pyrolysis experiments was subjected to leaching tests using 3 different leaching solutions: purified water, Ca $(NO_3)_2$ 0.1M and EDTA (ethyleneenediaminetetraacetic acid. All EDTA extractions from all the chars show percentages of metals in the extracting solution ranging from 5 to 35% depending on the production temperature of the char. However, these values are

lower than those obtained with a similar solution extracted from non-pyrolysed biomass. If EDTA extractions from different char types obtained at different pyrolysis temperatures are compared, a relationship between process temperature and metal availability is observed: the higher the temperature, the more resistant the metal compound in the char becomes to leaching.
From the comparison between EDTA extraction at the same temperature, it is possible to state that Zn is more predisposed to leaching and it is followed, in the order, by Cd and Pb. The classification is valid for all three process temperatures.
Steam is used as a pyrolyzing agent, as it affects the structural characteristics of char in a positive way (Ragucci et al., 2013). Because of the presence of steam, a final temperature of 873 K was selected for the experimental tests because this value lies on the borderline between pyrolysis and the gasification stage. The dependence of char properties on the process final temperature was assessed in the temperature range of 688–967 K, where no or limited release of the volatile fractions of PTEs in the gas phase is expected (Lievens et al., 2008b), with the aim of identifying the optimal process temperature that is a good compromise between weight reduction in the processed material and good chemical and structural quality of the solid residue.
From the conclusions drawn, it is clear that a more detailed experimental investigation is needed to obtain data on the dependence of heavy metal distribution in pyrolysis products obtained in different operating conditions and starting from different feedstock.

4. Materials and methods

The results presented in this thesis were produced by three separate experiments for every pyrolysis condition investigated. Three reliable replicates analysis were done for both the biomass and char samples.

4.1 Biomasses selected for phytoremediation

Biomasses for phytoremediation process are generally selected to match different desired parameters, such as absence from the trophic chain, high biomass production, ability to uptake heavy metals, high growing rate, high adaptability to the climatic conditions, and high resistance to biotic and abiotic stresses. Based on these criteria, the ECOREMED project selected five biomasses for phytoremediation tests, namely Populus nigra (P.nigra), Salix alba (S. alba) , Eucalyptus occidentalis (E. occidentalis), Fraxinus oxyphylla (F. oxyphylla), and Arundo donax (A.donax).

P. nigra is among the fastest-growing trees for SRC with an annual dry matter (d.m.) production of 17.8 Mg ha"1 y"1. Poplar trees, though not hyperaccumulators, are effective in uptaking PTEs from a very deep layer due to the efficiency of their root systems (Bhargava et al., 2012).

S. alba genus is a member of the Salicaceae family, including some of the shrub species currently being bred as a potential bioenergy feedstock, as the P. Nigra.

The Salicaceae family consisting of two genera with over 320 and 30 species, respectively, ranging from dwarf, alpine willows to shrubs reaching over 10 m, to trees greater than 20 m in height. All the tree hrubs are largely distributed in the cooler regions of the Northern Hemisphere.

E. occidentalis is a fast-growing source of wood largely used in the paper industry, producing residues that are potential candidates for pyrolysis. E. occidentalis was chosen also for its high d.m. yield (31.98 Mg ha"1 y"1) uptake of nutrients and heavy metals and salt tolerance (Fine et al., 2006; Quinn et al., 2015), as the groundwater of Litorale Domitio Agro Aversano NIPS is prone to salinization.

Another used for its productivity and adaptability to different environmental conditions of Mediterranean areas was F. oxyphylla (d.m. yield 17.3 Mg ha"1 y"1).

A. donax, fast growing herbaceous non-food crop, was selected for the high biomass productivity, high resistance and a high potential for invasiveness. A. donax spontaneously grows in temperate and subtropical regions and its uncontrolled proliferation requires frequent removal operations, particularly in urban areas. These operations involve significant costs due to the amounts of

biomass to be removed, and to the robustness and fibrous structure of its stems and rhizomes (Fernando et al., 2016). A. donax, was considered for phytoremediation, because it is a representative of the typical Mediterranean flora, and highly resist to biotic and abiotic stresses. Its high productivity (d.m. yield 15–30 Mg ha^{-1} y^{-1}) has been proven on marginal lands (Fagnano et al., 2015), and in polluted soils (Fiorentino et al., 2013, 2017). Moreover, the potential harvesting of belowground biomass (rhizomes with high stalk and nonstructural sugars content) could improve the added value of this crop.
Plants were transplanted in 2007 and harvested annually. The biomasses used for the pyrolysis experiments were obtained during the sixth growing cycle. No irrigation or fertilization occurred to reduce the energetic input to the cropping system. As expected, average biomass yield (13 t/ha d.m.) was lower than that obtained under high fertility conditions (Impagliazzo et al., 2016), but similar to yields harvested from other marginal lands (Fagnano et al., 2015).

4.2 Contaminated Biomasses after phytoremediation: Populus Nigra and Arundo Donax

On the basis of the results obtained from the preliminary study of pyrolysis as post treatment for the valorization of contaminated plants, three biomasses were selected for the phytoremeditation tests, P. nigra, E. occidentalis and A. donax. Populus and A. donax were planted on contaminated ex-industrial site located in Campania region, while Eucalyptus was cultivated on a contaminated ex-agricultural site.
Soils in the area are characterized by the presence of both detrital-alluvial sediments and the fall of pyroclastic material from ‘Campi Flegrei’. Furthermore, the intensive agriculture and livestock, the presence of numerous dumping sites (both legal and illegal), the usual practice of waste incineration and the common sewage network leakage, has produced groundwater and soil contamination, with many wells showing very high nitrate concentration and soil pollution by PTEs, hydrocarbons and pesticides. The content of PTEs defined as priority pollutants by the Italian legislation (D. Lgs 152/2006) was measured. The metals analysed in this study were selected on the basis of the results of the sampling carried out on contaminated sites involved in the project. The site resulted polluted by Cu, Zn, Pb and Cd as reported in the study of Rocco et al. (2016).

4.3 Feedstock characterization

The harvested biomass was pre-dried on forced air ventilated racks to avoid fermentation. The moisture content at harvesting ranged between 57.3 and 53.7 wt%, whereas the moisture content after forced air ventilation was greatly lower. In both cases, the moisture content was determined by drying the samples in a thermo-ventilated oven at a temperature of 105 °C until a constant weight was reached. All the pre-dried biomass samples were completely dried in an electric oven at 105 °C for 2 h to remove the residual moisture before the pyrolysis tests.
All the biomass samples were milled in a blade shredder and the sieved fractions in the 400–600 lm size range were collected for characterization and the pyrolysis tests. In all the examined cases, this fraction accounted for 80–85 wt% of the ground-up sample, thus assuring the fraction was representative of the raw feedstock.

- The ultimate and the proximate analyses of the samples were performed using a CHN 2000 LECO analyser with EDTA as the standard and a TGA 701 LECO thermogravimetric analyser, respectively, based on CEN/TS 15104 and ASTM E870 procedures. The higher heating value (HHV) of the biomass samples was calculated, based on its elemental composition on a dry basis, using the Dulong-Berthelot formula (Channiwala and Parikh, 2002). The complementary value to 100 is the

- The content of major inorganic elements was determined by dissolving the biomass samples via microwave-assisted acid digestion based on US-EPA Methods 3051 and 3052. A representative sample (200 mg) of biomass was dissolved in 10 ml 65% nitric acid and 1.5 ml H_2O_2. The vessel was sealed and heated in the microwave unit at 140 C for 10 min, then 180 C for 30 min (maximum power 1000 W). After they were cooled, the digested samples were analysed by inductively coupled plasma mass spectrometry (ICP/MS) using an Agilent 7500CE instrument.

- The content of extractives was determined according to the NREL/TP-510-42619 procedure using water and ethanol for the determination of hydrophilic extractives and hexane as extracting solvent for hydrophobic extractives. Holocellulose content was obtained according to the sodium chlorite method (Rowell, 2012); hemicellulose content has been determined according to the method described in Yang et al. (2006), while lignin content has been obtained following the NREL/TP-510-42618 procedure.

- In the case study of Eucalyptus under different temperature, the FTIR spectra of the feedstock and of the char obtained at T = 967 K were analyzed in order to have information of the modifications to the biomass chemistry when it was exposed to high temperatures. Infrared spectra of the samples were recorded on a Nicolet iS10 spectrophotometer using the attenuated total reflectance (ATR) method. The ATR method allowed the samples to be analyzed as powder and, differently from the transmission mode, did not require mixing with KBr. The ATR infrared spectra were recorded in the 650–4000 cm 1 range by using a zinc selenide crystal, collecting 32 scans, and correcting the background noise. The spectra were acquired and processed using OMINIC 8 software.

4.4 Results on not contaminated biomasses

Table 4.1 reports the results of the characterization of feedstock grown on not contaminated soils used for the preliminary pyrolysis tests.
The biomass samples did not exhibit large variations in the elemental and proximate analysis. Even though ash content varied slightly (the highest values were for S. alba and A. donax), remarkable differences occurred in the ash composition reported in Table 4.1.
Despite having the highest ash content, A. donax had the lowest content of Na, Ca, and P. The high content of ash may be due to the presence of SiO_2, which is not detectable with the demineralization procedure adopted in this study. Nevertheless, previous data (Nassi o Di Nasso et al., 2010) suggest that SiO_2 accounts for almost 40% of ashes contained in the culms of A. donax harvested annually until the seventh year of growth.
For all the other biomasses Ca was the main ash component followed by K, Na and P. Na was particularly abundant in E. occidentalis wood. Unusually, high Al content was observed for all the biomasses, except for A. donax, probably because of the presence of bark typically richer in inorganics (Biomass Combustion and Cofiring, 2016). In order to understand and interpret the results on char is important to determine the biochemical composition of biomass. The hemicellulose, cellulose, and lignin content were obtained differently for all biomasses.
The cellulose content varies considerably, from 28% for Salix to 55% in P. nigra. Conversely, the hemicellulose was higher in Salix, Fraxinus, and A. donax and lower in E. occidentalis. The biomass with the low lignin content was the P. nigra. In the case of elemental and biochemical analysis the complementary value to 100 is the ash content, reported in Table 4.1 (Section Proximate Analysis).

Biomass	***P***	***S***	***F***	***E***	***AD***
			*Elemental analysis		
			wt % db		
C	47.6 (<0.5)	46.7 (<0.5)	47.8 (<0.5)	46.8 (<0.5)	44.5 (0.5)
H	5.5 (1.5)	5.3 (1.1)	5.6 (1.9)	5.4 (2.2)	5.4 (<1)
N	0.0	0.5 (<0.5)	0.6 (<0.5)	0.0	0.0
S	0.1 (<0.5)	0.1 (<0.5)	0.2 (0.5)	0.1 (<0.5)	0.2 (<1)
O	44.1 (<1)	42.2 (<0.5)	44.4 (<1)	45 (<0.5)	43.1 (<0.5
			Higher Heating Value calculated		
			MJ/kg db		
HHV	18.8 (1.6)	18.4 (1.2)	18.6 (<1)	18.3 (1.5)	17.7 (<1)
			Proximate analysis		
			wt % as recived		
moisture	7.6 (<1)	7.8 (1.2)	9.43 (1.4)	8.4 (<1)	4.6 (<1)
			wt % db		
volatiles	79.8 (1.7)	75.4 (<1)	79.8 (<1)	79.9 (1.4)	75.8 (<1)
fixed carbon	16.3 (1.8)	18.03 (1.2)	16.17 (<1)	15.9 (1.2)	16.6 (1.5)
ash	2.6 (2.2)	5.1 (<1)	2.3 (<0.5)	2.7 (1.2)	6.8 (<1)
			Ash composition analysis		
			mg/kg db		
Na	2400 (11)	3698 (9)	3928 (8)	11140 (9)	86.94 (12)
Al	1040 (5)	6646 (13)	1232 (12)	1142 (9)	106.1 (3)
P	1150 (2)	1870 (4)	1566 (2)	1720 (2)	652.05 (3)
K	3523 (1.2)	8057 (3)	7026 (5)	5709 (8)	10695.26 (1
Ca	8642 (1.8)	12820 (<1))	6801 (<1)	14250 (2)	1014.3 (1)
Mg	276.3 (15)	320.9 (<1)	183.8 (<0.5)	212.3 (12)	340.266 (<
Fe	301.8 (18)	987.2 (16)	284.5 (12)	280.1 (12)	114.09 (9)
			*Biochemical composition		
			wt % db		
extractives	3.6 (<1)	4.8 (<0.5)	8.7 (<0.5)	18.9 (1)	6.5 (2)
hemicellulose	26.8 (2)	35.8 (1.1)	32.1 (1)	17.7 (2)	28.2 (2)
lignin	11.6 (1)	26.2 (1.2)	13.2 (<1)	19.9 (1.2)	19.7 (2.5)
cellulose	55.4 (1.2)	28.1 (1)	43.7 (1.4)	40.8 (1.1)	40.5 (1.2)

*Table 4.1: Feedstock characterization: Populus nigra L. (P), Salix alba L. (S), Fraxinus oxyphilla Bois. (F), Eucalyptus occidentalis Endl. (E) and Arundo donax L. (AD) *By difference, ash content taken into consideration. SD is given in brackets.*

4.5 Results on contaminated biomasses

The study on contaminated biomasses was conducted on different plant parts, conversely to the study of the first section.
Several studies proved that that heavy metals accumulate in actively growing tissues such as sprouts, roots and leaves. The zinc and cadmium concentrations are highest in the foliage. (Lievens et al., 2009) The highest copper, lead, and chromium concentrations were measured in the trunk of willow species grown in sludge-treated soil, while zinc, cadmium, and nickel were accumulated mostly in the foliage (Pulford and Watson, 2003). The trunks and branches are used to transport heavy metals between the roots and leaves of the plant, thereby are less contaminated.
The three biomasses from phytoremediation were divided into different parts.
On the basis of the ICP/MS, the E. occidentalis has not accumulated heavy metals, so it was not studied in the second part.
The P. nigra was classified into branches and leaves, while the A. donax in rhizomes (underground organs next to the roots) and culms.
In the Table 4.2 the results of elemental and proximate analysis and HHV calculation are listed for contaminated biomass.
Hydrogen content doesn't exhibit large variations between leaves and branches, whereas the content of carbon and oxygen was lower in the leaves due to the presence of large amount of ashes. Nevertheless, the O/C and H/C atomic ratio was 0.69 and 1.48 for branches and 0.62 and 1.38 for the leaves because of the lower content of carbon on dry ash free basis in the branches. This result allowed postulating a higher content of holocellulose in the branches. It was well known that the relative content of cellulose, hemicellulose and lignin determines a different pyrolytic behavior and different characteristics of the final solid residue (Giudicianni et al., 2014). Rhizomes and culms were characterized by carbon content similar to the values of non-contaminated arundo. Culms and rizhomes were characterized by a different carbon and nitrogen content. The fixed carbon and ash contents were higher in rhizomes than in culms.

Biomass	***Populus nigra***		***Arundo donazx***	
	branches	***leaves***	***rhizomes***	***culms***
	*Elemental analysis			
	wt % db			
C	47.7 (<1)	41.5 (1.1)	42.61 (<1)	44.6 (<1)
H	5.9 (1)	4.8 (1)	5.6 (<1)	5.8 (<0.5)
N	0.0	1 (<1)	1 (7.5)	0.5 (23)
S	0.1 (<1)	0.1 (<1)	-	-
O	44.2 (2.1)	34.7 (1.4)	49.6 (<1)	48.3 (<1)
	Higher Heating Value calculated			
	MJ/kg db			
HHV	19.4 (1.2)	16.8 (1.6)	16.4 (<1)	17.6 (1.2)
	Proximate analysis			
	wt % as recieved			
moisture	7 (<1)	8.7 (1.4)	1 (<1)	0.82 (1.2)
	wt % db			
volatiles	79.9 (2.6)	66.6 8 (2.1)	68.1 (<1)	75.4 (<1)
fixed carbon	18 (1.6)	15.5 (1.3)	30.8 (1.2)	23.6 (1.4)
ash	2.2 (2.1)	18 (<1)	1.1 (<0.5)	0.9 (<1)
	Ash composition analysis			
	mg/kg db			
Na	206 (52)	573 (9)	266 (<1)	258 (<1)
Al	248 (119)	1854 (11)	2317 (<0.5)	28 (<1)
P	468 (<1)	1088 (10)	3458 (<1)	3182 (<1)
K	4477 (2)	3596 (4)	13566 (<0.5)	9052 (<0.5)
Mg	836 (7)	2325 (10)	1194 (<1)	818 (<0.5)
Ca	9407 (6)	37500(5)	1440 (<0.5)	540 (<1)
Fe	132 (78)	783 (2)	2290 (<1)	43 (<0.5)
Cl	58 (<1)	39 (<1)	111 (<1)	87 (<1)
Cd	2 (5)	10 (7)	8 (<1)	0.15 (<0.5)
Cu	8 (18)	63 (9)	0.3 (<1)	0.2 (<1)
Pb	60 (5)	423 (1)	17 (<0.5)	0.4 (<1)
Zn	50 (9)	118 (6)	140 (<1)	87 (<1)

*Table 4.2: Feedstock characterization: Populus nigra L. (branches and leaves), and Arundo donax L. (rhizomes and culms). *By difference, ash content taken into consideration. SD is given in brackets.*

The concentrations of the major inorganic elements and of the heavy metals have been reported in Table 4.2. The PTEs accumulation was not homogeneous in the plants. Cd, Cu, Pb and Zn have been detected in all the samples, but leaves were characterized by the highest concentration of all the contaminants. This finding was consistent with previous literature data on Populus used for phytoremediation (Rafati et al., 2011). Pb concentrations was higher in the Populus leaves, than in the branches, as well as in rhizomes than the culms.

4.6 Experimental set-up: pyrolysis reactor

The experimental tests of this thesis were conducted with the pyrolysis system available at Institute of Research on Combustion, C.N.R., designed with the aim to allow the effective control of the thermal conditions in the reaction chamber, thus reducing the variability in the data by avoiding potential bias due to mass transport, sample preparation and heat transfer. Therefore, with this configuration it is possible to have an accurate study on devolatilization of the single components of the biomasses during the process. This configuration leads to have a flexible use of the feedstock, and its size (pellets, chips or powder), pyrolyzer agent (steam, nitrogen, CO_2 and mixture gas) and temperature.

In the following sections a detailed description of the experimental apparatus and of its design criteria is given.

The experimental set-up, showed in Figure 4.1, consists in a steam generator followed by a super heater equipped with a programmable controller to control steam heating rate, a jacketed reactor, a condensation device, a liquid collection system and a gas sampling station.

All parameters are monitored during the test by means LabVIEW software interface.

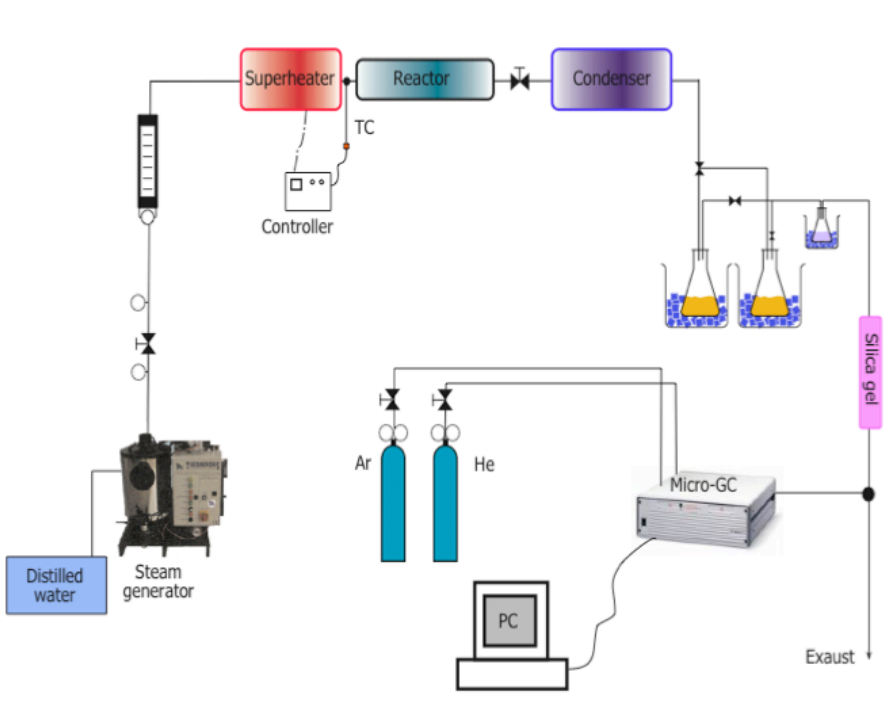

Figure 4.1: Experimental pyrolysis set-up of the laboratory of IRC-CNR.

The reactor consists of a jacketed prismatic chamber in which the sample of biomass is spread in thin layers over 4 trays along the rectangular cross-section of the inner reaction chamber.
Sample tray plates are placed uniformly along the rectangular cross-section (internal dimensions: width = 0.04 m, height = 0.052 m, length = 0.02m) of the reaction chamber at 0.02 m from the ceramic flow straightener placed at the inlet of the chamber.
The dimensions of the sample trays (width = 0.04 m, length = 0.113 m) have been determined so that the biomass sample could be spread on the trays in a thin layer (approximately 1 mm thick), in order to allow an effective control of the thermal conditions in the reaction chamber.
The biomass is grinded finely (sample size d<600 m) in order to limit the intraparticle thermal gradient during the process and placed on a tray in the way of a monolayer to avoid heat transfer resistance related to a packed bed configuration. Biomass sample is 1.5 g spread on each tray plate.

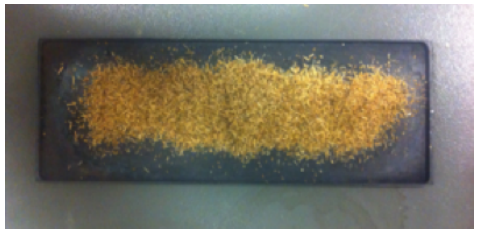

Figure 4.2: Sample trays and feedstock.

The reactor and the trays are made up of Fecralloy®. The dimensioning of the flow straightener (thickness = 0.014 m; cell diameter = 0.0016 m) has been made considering the minimum pressure loss able to assure a uniform distribution of the air-flow velocity at the inlet of the chamber evaluated by mean of an extensive fluid-dynamical simulation (Giudicianni et al, 2010).

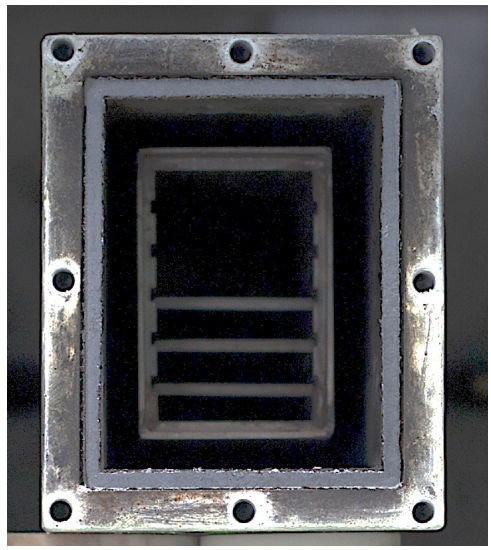

Figure 4.3: Cross section of the reaction chamber.

To limit external heat loss the reactor chamber is jacketed so that the steam flows in the jacket, equipped with baffles to allow a uniform air distribution and, hence, a final velocity and temperature of the flow, before reversing its flow to enter the reaction environment through a ceramic flow straightener. Heating panels, covered by a layer of insulating panels, surround the external jacket.

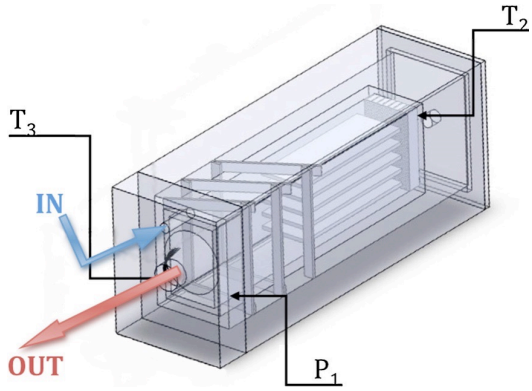

Figure 4.4: 3D view of the reactor (Ragucci et al, 2013).

The internal part of the lid is provided with one 'N-type' thermocouple (T_2) able to measure the temperature in the middle point of the reactor chamber. A thermocouple the 'type N' is also placed in the reactor jacket, just before the flow straightener, to measure temperature and control heat flux to the steam super heater (T_3).

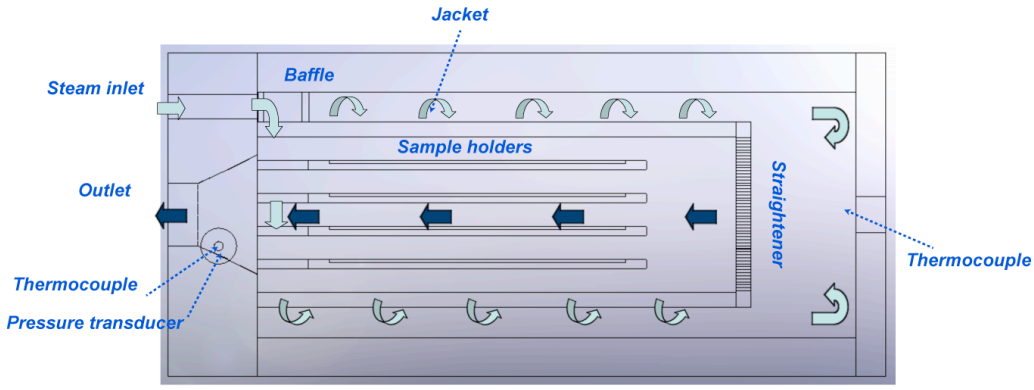

Figure 4.5: Reactor longitudinal section

The thermocouple type N (NiCrSi-NiSi) is used in applications with greater resist and stability are required. With diameter 1.5 mm is similar to the thermocouple "type K" characterized by the same operating temperature range (ASTM E230: -270-1260°C), tolerance (±2,2 °C or ±0,75 %) and sensibility (41 µV/°C). The advantage is the addition of silicon to wires which leads to a good de-sensibilization to phenomenon of the "green-rot". The "green-rot" is the phenomena by means the atmospheres facilitate corrosion of the positive thermoelement (chrome) at low oxygen percentages and causes calibration problems at high temperatures. This kind of thermocouple is suitable for the steam pyrolysis conditions avoiding them corrosion.
Temperature and pressure are monitored also at the exit of the reaction chamber where a thermocouple and a pressure transmitter are placed. During the pyrolysis, the pressure inside the chamber is on average 4.5 bar. In the Figure 4.6 is illustrated the pressure profile of a generic trial. The trend is confirmed the by the replicated tests. Steam heated to the programmed temperature in a super heater enters the reaction chamber and invests tangentially the biomass samples. At the test chamber's outlet, a needle valve is used to regulate the mass flow rate and ensure the proper backpressure in the chamber.

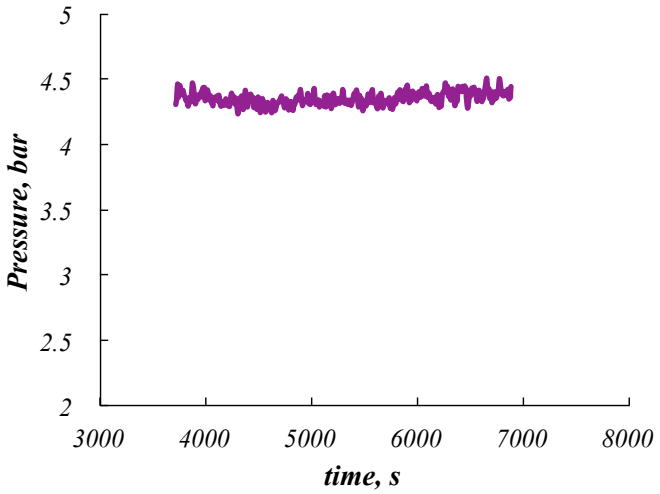

Figure 4.6: Pressure profile

The mass flow rate is maintained at 0.25 g/s during the tests, corresponding to an average residence time of 1.5–3 s for the gas phase in the reactor, depending on the reactor temperature. The gaseous stream exiting the reaction unit is condensed and collected, whereas non-condensing gases are fed to the analytical system for on-line characterization. The volatiles produced in the reaction unit entered the condensation device, which consists of a jacketed coil where condensable volatiles cool and condense. At the condenser's outlet, a Pyrex flask submerged in a 273 K thermostatic bath collected the condensed volatiles. A stream of N_2 at a constant flow rate (0.0139 L/s) is also injected at the inlet of the condenser to drive the non-condensable gases from the condenser to the gas sampling point. Permanent gases flowed into a silica gel trap, where their moisture content is reduced before they are sampled and analyzed. The gas composition, in terms of the volume percentage of the major gas species (CO, CO_2, H_2, CH_4, C_2H_6, C_2H_4 N_2 and O_2), are measured by a gas chromatograph equipped with a thermal conductivity detector (Agilent 3000 Quad) every 171.5 s. In the trial phase of each test run, biomass samples were heated in a nitrogen atmosphere from ambient temperature up to 383–373 K. In this temperature range, the nitrogen was replaced by steam, which was heated up to the final temperature. A constant nitrogen flow rate (0.0139 L/s) is ensured during both the heating phase and system cooling at ambient temperature, immediately after the programmed final temperature is reached. Consequently, the pyrolysis time depends on the final temperature considering that heating rate is maintained constant at 4 K/min.

4.7 Determination of products yields

The yields of the pyrolysis products were determined as follows.

To provide a detailed chemical analysis, the outlet stable species were analysed by gas chromatograph. Gas production, expressed as volume of gas per gram of fed biomass, was calculated, starting from the temporal profiles of all the gaseous species of interest (CO, CO_2, H_2, CH_4, C_2H_6, C_2H_4, N_2 and O_2). The gas was sampled every 171.5 s and its volumetric composition analyzed using a gas chromatograph equipped with a thermal conductivity detector (Agilent 3000 Quad). The analytical device allows to perform fast analysis (analysis time less than 160 s) directly at the sampling point. It is made up of two independent channels each one equipped with a specific capillary column to allow the simultaneous detection of all the species of interest. Column Plot U has been selected to detect CO_2, C_2H_6 and C_2H_4, using helium as carrier gas, while column Molsieve 5A equipped with pre-column Plot U allow the detection of CO, H_2, N_2 and O_2 using argon as carrier gas. Each channel is equipped with a Thermal Conductivity Detector (TCD) detector, sensitive enough to detect ppm-level concentration of target species. Stable species were identified by the determination of their individual retention times and calibration were made directly using cold-gas mixtures. For the gas-mixtures at low and high concentrations, maximum relative errors in mole fractions are estimated to be ± 10% when the concentrations approach the detection threshold, which is about 1 ppm for species analysed. Experiments were performed at least twice under all test conditions to ensure measurement reproducibility.
The volumetric concentration of each species calculated on N_2 basis, was multiplied by the N_2 flow rate, to obtain the corresponding volumetric releasing rate curve. The total volume of each gaseous species was calculated by integrating the corresponding releasing rate curve along the test period, and the total gas production was finally obtained by summing the production of each gaseous species, then dividing by the mass of the fed biomass. Gas weight composition was obtained from the volumetric composition, by adopting the ideal gas law at the conditions of the sampling point (P = 1 atm, T =298K). The HHV of the gaseous product was calculated, based on its chemical composition. The liquid phase was collected in two distinct fractions and, collected and analysed separately.

- Liquid condensed on the walls of heat exchanger coil, made up mainly of non-polar light organic compounds and heavy aromatic compounds;
- Polar fraction of liquid collected in the catch pots highly diluted in condensed water.

The two fractions will be examined with different analytical techniques on the basis of their own chemical nature for subsequent analyses, not reported in the present thesis.
Char yield was determined gravimetrically with respect to the fed sample, whereas liquid yield was evaluated as the amount needed to complete the mass balance.

4.8 Char characterization

Char samples were characterized in terms of elemental and proximate analysis according to the ASTM D5373 and ASTM D1762-84 procedures, following the same procedure performed for the feedstock (see section 5.3). The Dulong formula was also used to determine the char's HHV, based on its elemental composition.

- Char pH was measured with a digital pH meter (827 pH LAB, Metrohm) in deionized water using a 1:20 wt/wt ratio following the ASTM D4972-13 standard procedure.

- The content of major inorganic elements and the PTEs was determined by ICP/MS applying the procedure described in detail in Section 5.3 (Feedstock characterization), by dissolving the biomass samples via microwave-assisted acid digestion based on US-EPA Methods 3051 and 3052. The results were reported in terms of content of the inorganic species and of ion recovery in the char. The first is intended as mass of ion per mass of char and is used to calculate the ion recovery by multiplying it by char yield and dividing by the mass of ions in the raw biomass. The Cl content in feedstock and in char samples was determined in according to the CEN/TS 15289 procedure.

- Characterization of the char samples' pores, was carried out by applying gas adsorption porosimetry. Sorption/desorption isotherms were obtained using argon at 87 K as the adsorbate in an Autosorb-1 (Quantachrome) apparatus. Before analysis, the samples were degassed at 573 K for 5 h under vacuum conditions. The surface area was evaluated using the BET equation. The Brunauer-Emmett-Teller (BET) method is the most widely used procedure for the determination of the surface area of solid materials and involves the use of the BET equation.

$$\frac{1}{W\left(\left(\frac{P_0}{P}\right)-1\right)} = \frac{1}{W_m\, C} + \frac{C-1}{W_m\, C}\left(\frac{P}{P_0}\right)$$

Eq. 1: Brunauer-Emmett-Teller (BET) equation.

W is the weight of gas adsorbed at a relative pressure, P/P_0, and W_m is the weight of adsorbate constituting a monolayer of surface coverage. The term C, the BET C constant, is related to the energy of adsorption in the first adsorbed layer and consequently its value is an indication of the magnitude of the adsorbent/adsorbate interactions.
The determination of micropore volume and area was performed using the "t-plot method" in according to the procedure ASTM D5816. The total pore volume of the samples was determinated using the "BJH method", whereas the mesopore volume and area were obtained for calculation. The first one was calculated for difference between total pore volume of the sample and the micropore volume; the second one was calculated for difference between the BET and the micropore surface area.

4.9 Leaching tests

The metal availability was determined through the leaching test on chars, as reported in Gonsalvesh L. et al. (2016). The extraction procedure was conducted in parallel batch mixing 500 mg char with 5 mL of solution for 24 h under constant stirring. Three solutions were used to have information on extractability of the metals: extraction with purified water (Milli-Q water); extraction with 0.1 mol L−1 solution of $Ca(NO_3)_2$ (Sigma Aldrich); extraction with 0.02 mol L−1 solution of EDTA (Sigma Aldrich) buffered at pH 4.65 with 0.5 mol L−1 NH_4Ac and 0.43 mol L−1 HAc. Afterwards the samples were centrifuged for 2 min at 3000 rpm (Universal 320, Hettich Lab Technology). Prior to ICP-MS analyses, the supernatant was filtrated on a 45 μm Celluse Acetate filter (Millipore).

Data are presented as mean values of three replicates with relative standard errors.

5. Results and discussion

5.1 Feedstock from marginal lands

This chapter describes the results of the experimental investigation of slow pyrolysis of biomasses chosen for the preliminary phytoremediation test. The influence of the feedstock and temperature are discussed on the development of the main gaseous species (CO, CO_2, CH_4 and H_2) and on the physico-chemical characteristics of the chars.

In this section is reported:

- the critical analysis of the effect of the final temperature on Eucalyptus yields, and the characteristics of the chars, in the temperature range 688-977 K, namely 688, 794, 873, and 967 K;

- the comparison of the product yields and characteristics of Populus nigra, Salix alba, Fraxinus oxyphylla, Eucalyptus occidentalis and Arundo donax at the final temperature of 873K.

This chapter is based on the article submitted to scientific journals:
"*Pyrolysis for exploitation of biomasses selected for soil phytoremediation: Characterization of gaseous and solid products*" by Giudicianni P., Pindozzi S., Grottola C.M., Stanzione F., Faugno S., Fagnano M., Ragucci R. published in Waste Management (2017).
The yields variation of the pyrolysis product is first presented. Then, the temperature dependent physicochemical characteristics of char are discussed. Finally, chars obtained from different feedstocks at T = 873 K are compared. The effect of pyrolysis temperature was studied using E. occidentalis as the reference biomass, because of its high biomass yield, ability to uptake nutrients and heavy metals tolerance. Moreover, in view of the possibility of valorizing the char obtained by the biomass post-processing treatment, E. occidentalis appears to be a good candidate for pytoremediation process on the ground of literature data on the characterization of char obtained from N_2 assisted pyrolysis under thermal conditions similar to the ones experienced by the biomass samples in this study. Martins at al. (2007) and Abdullah et al. (2010) showed that chars obtained from Eucalyptus have a very high carbon content in all the explored temperature range from 573 to 1173 K, thus showing a high HHV even at low temperature (Abdullah et al., 2010). Furthermore, this choice has been supported also by data from Guerrero et al. (2008) showing high values of BET surface for char produced from Eucalyptus undergoing to nitrogen assisted slow pyrolysis at 873 K.

5.2 Slow pyrolysis of Eucalyptus occidentalis: T= 688-976 K

Figure 5.1 shows the yield of products at different final temperatures. In the examined temperature range, 688–967 K, char yield decreased from 37.1 to 18.3 wt%, whereas gas production increased from 0.07 to 0.64 $Nm^3/kg_{biomass}$. The reduction in liquid yield with increased temperature is negligible, as it remains stable at approximately 50 wt%, which agrees with the literature that shows that, in slow pyrolysis conditions, the production of condensable products is mostly completed at approximately 700 K (Di Blasi, 2009).

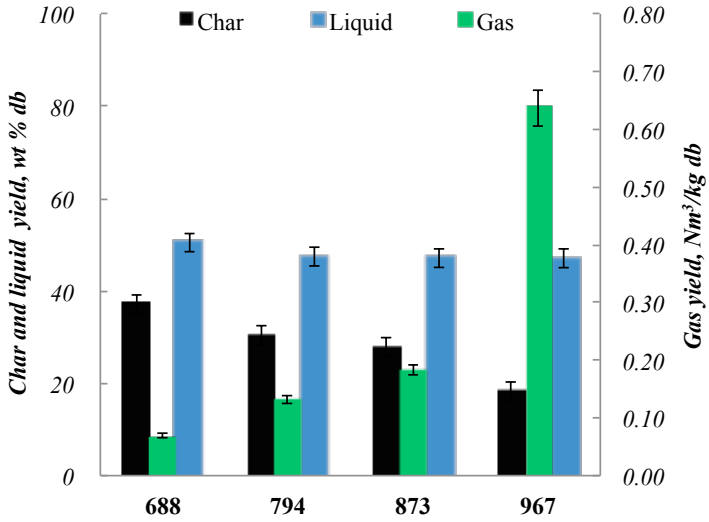

Figure 5.1: Products yield from E. occidentalis as a function of temperature.

To elucidate the evolution of E. occidentalis during the thermal treatment, Figure 5 reports the releasing rate of the main gaseous species up to 967 K, and 5.1 reports the gas composition, HHV of the gaseous product, and energy recovery (ER) calculated as the percentage of the HHV of the initial biomass recovered from the gaseous product.

Biomass	CO_2	CO	CH_4	H_2	HHV	ER
		wt %			*MJ/kg*	*%*
P	77.3	15.6	5.3	1.9	7.2	7.7
S	82.0	11.4	4.7	1.9	6.5	8.5
F	83.2	10.5	4.2	2.0	6.3	9.2
E	81.1	12.6	4.7	1.6	6.1	8.1
AD	74.2	19.4	5.1	1.1	6.3	6.4

5.1: Composition and properties of the gaseous product from pyrolysis of Eucalyptus at different final temperatures.

The CO_2 concentration was lowest at 873 K, whereas the concentrations of CO and CH_4 reached their maximums at the same temperature. On the contrary, the content of H_2 increased throughout the examined temperature range. Both HHV and ER increased as temperature increased, ranging respectively from 1.8 to 8.8 MJ/kg and from 1.2 to 28.9%.

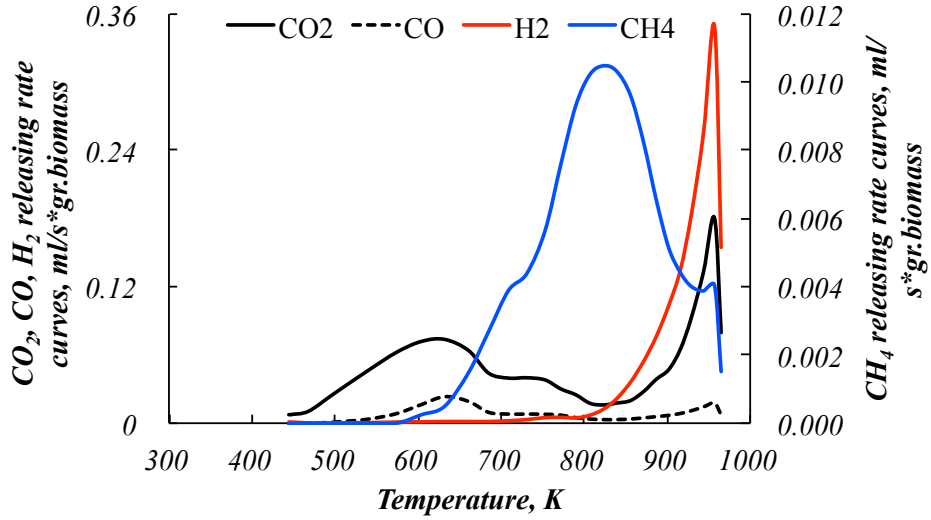

Figure 5.2: Releasing rate (ml s 1 g 1 biomass on daf basis at STP conditions) of gaseous species from E. occidentalis as a function of temperature.

As shown in Figure 5.2 it is possible to observe that the devolatilization of the biomass sample started at approximately 420 K. The release of CO_2 and CO in the low temperature range (420–688 K) corresponds to the chemical bond rupture of the carboxylic and carbonyl groups in the holocellulose fraction, whose devolatilization produces mainly condensable species (referred to in Figure 5.1 as ‘‘liquid”) allowing for high liquid yield even at low temperature (50.5 wt% at T= 688K). At 688 K, gas production was still very low (0.07 $Nm^3/kg_{biomass}$) as well as calorific value and ER, due to the high content of CO_2. At this temperature, char yield was still high (37.1%), but it decreased with increasing temperature up to 794 K and then more slowly at 873 K, even though liquid yield remained relatively unchanged, indicating that the release of condensable species could be considered already concluded at 688 K. The release of CO_2, CO, CH_4, and H_2 in the temperature range of 688–873K (mainly due to the secondary decomposition of condensable species entrapped in the solid matrix and to primary degradation of lignin) is responsible for the slight increase in gas yield. The production of CH_4, and H_2 determines the increases in HHV and ER. In the temperature range of 873–967 K, due to the presence of steam in the reaction environment, char gasification reactions occurred which

caused a rapid increase in the CO_2 and H_2 releasing rates, an increase in H_2 content of the gaseous product, and a reduction in char yield to 18.3%. A substantial improvement in gas energetic potential was observed at 967 K with ER attaining almost 29%.

5.3 Slow pyrolysis at Tf= 873 K: product yields

In the Figure 5.3 are represented the yields of pyrolysis products of different biomass samples at 873 K.

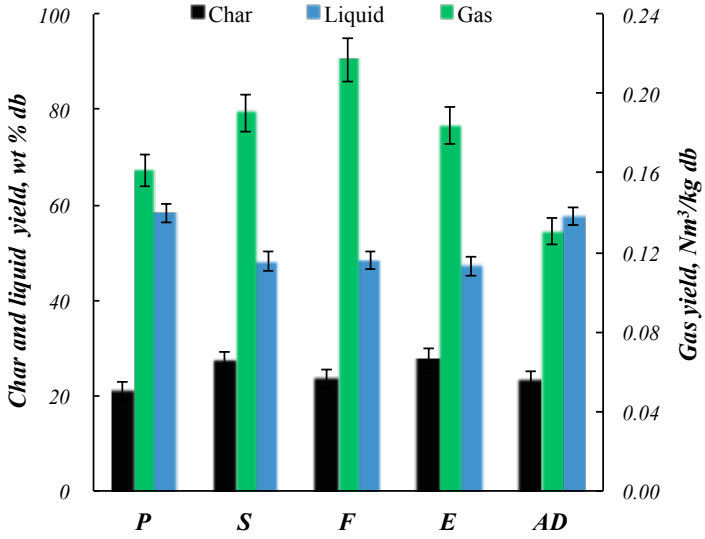

Figure 5.3: Yields of pyrolysis products at T = 873 K calculated on biomass db.

Liquid is the main product for all the tested biomasses and its yield was highest for P. nigra (58.3 wt%) and A. donax (57.6%), whereas lower and comparable values were obtained for S. alba, F. oxyphylla, and E. occidentalis. Gas production varied between 0.13 and 0.22 $Nm^3/kg_{biomass}$, being highest for F. oxyphylla followed by S. alba, E. occidentalis, P. nigra and finally A. donax. These results cannot be trivially correlated with biomass biochemical composition, except for P. nigra where the high liquid yield and low gas production are consistent with its high cellulose content, 55.3% wt on dry basis (Giudicianni et al., 2015), measured following the procedure described in Yang et al. (2006).

S. alba and E. occidentalis provided the highest char yields, 27.2 and 27.8wt% respectively, whereas a lower char yields were obtained from F. oxyphylla and A. donax (approximately 23 wt%) and the lowest yield was from P. nigra (20.9 wt%). This result is unexpected if one considers the biochemical composition of the original biomasses on dry basis (see section 5.1 c), Table X). Indeed, char yield depend on many factors. First of all it is dependent on the lignin content of the biomass because, among the main organic biomass components, lignin is the one that contributes more then the other ones to the production of char (Giudicianni et al., 2013).

Many authors suggested that alkali and earth alkali metals affect char yields because they catalyze cellulose decomposition (Shimada et al., 2008; Patwardhan et al., 2010; Gargiulo et al., 2015; Das and Sarmah, 2015a). When cellulose devolatilization occurs in presence of such inorganics transglycosylation that leads to the formation of heavier condensable species is depressed with respect to ring fragmentation producing gas and light condensable species. In agreement with this mechanism higher yields of char and lower yield of liquid are produced. Nik-Azar et al. (1997) suggested that sodium and potassium are stronger cracking catalysts than is calcium, whereas, in a recent study, Shimada et al. (2008) reported that both alkali and alkaline earth metals significantly influence the formation of low molecular weight compounds. As the catalytic action affects cellulose decomposition pathway the influence of alkali and earth alkali metals is the more remarkable the higher is the cellulose content.
Figure 5.2 reports the gas composition, HHV of the gaseous product, and energy recovery (ER) calculated as the percentage of the HHV of the initial biomass recovered from the gaseous product. As it can be seen from Table X, CO, CH_4, and H_2 were the main combustible constituents of the gaseous product characterized by a high level of dilution in CO_2 (74.2–83.2 wt%).

Biomass	CO_2	CO	CH_4	H_2	HHV	ER
		wt %			*MJ/kg*	*%*
P	77.3	15.6	5.3	1.9	7.2	7.7
S	82.0	11.4	4.7	1.9	6.5	8.5
F	83.2	10.5	4.2	2.0	6.3	9.2
E	81.1	12.6	4.7	1.6	6.1	8.1
AD	74.2	19.4	5.1	1.1	6.3	6.4

5.2: Composition and properties of the gaseous product from pyrolysis of different biomasses at T = 873 K.

Gas obtained from P. nigra and A. donax had the lowest CO_2 content. However, the highest H_2 and CH_4 contents in gas from P. nigra are responsible of its highest HHV. The highest ER was from F. oxyphylla, due to the enhanced gas production. For all the tested biomasses, the energy recovered in the gaseous mixtures was always lower than 10% due to the low HHV ranging from 6.1 to 7.2 MJ/kg. Low values of HHVs make the use of these mixtures difficult in traditional combustion systems because of flame instabilities, thus requiring the addition of auxiliary conventional fuels. Nevertheless, it has been demonstrated that the direct use of raw pyrolysis gases is feasible under Mild (moderate or intense low-oxygen dilution) combustion conditions (Cavaliere and de Joannon, 2004; Sabia et al., 2016). In this kind of combustion, the reactive process evolves from very diluted reactants, as the pyrolysis gas can be, at a

temperature higher than the autoignition temperature of the fuel itself (Cavaliere and de Joannon, 2004), thus not requiring high HHV fuel gas to sustain the combustion process. In this context, ER, rather than HHV, should be considered when choosing the fuel to be fed to the combustion process. Results obtained in the present study reveal that F. oxyphylla was preferred for the application of the gas as fuel in Mild combustion systems, as it had the highest gas production and ER.

6. Char characterization

6.1 Influence of temperature

In agreement with previous findings (Zanzi et al., 2002; Lee et al., 2013; Das et al., 2015c; Srinivasan et al., 2015), data obtained in the present study show that thermal conditions during pyrolysis remarkably affected the char properties.

T, K	O/C	H/C	HHV	ER	volatiles	fixed carbon	ash
			MJ/kg	%	wt % dry basis		
688	0.28	0.48	22.9	40.2	41.7	49.9	8.4
794	0.14	0.38	26.5	40.9	32.3	57.8	10.0
873	0.09	0.28	28.0	40.6	24.3	64.3	11.4
967	0.13	0.17	24.2	19.2	22.7	61.3	16.0

6.1: Composition and properties of Eucalyptus char obtained at different pyrolysis temperatures.

Table 6.1 shows the characterization of char obtained from pyrolysis of E. occidentalis at different final temperatures. O/C and H/C ratios were used to assess the degree of aromaticity and maturation during pyrolysis. The O/C ratio decreased rapidly from 0.72 in the raw sample to 0.28 in the char obtained at 688 K. As observed for the gas, most of CO, CO_2, and condensable compounds were released from the holocellulose fraction at temperatures lower than 688 K. The devolatilization of oxygenated compounds creates a substantial reduction in oxygen content, thus explaining the low O/C ratio, even at low temperature. As the temperature increased up to 873 K, the O/C ratio continued to decrease with a trend reversal occurring between 873 and 967 K, due to the onset of char oxidation reactions. On the contrary, the H/C ratio steadily decreased as the temperature increased, from 1.38 in the raw biomass to 0.17 in the char obtained at 967 K, indicating an increase in unsaturated C bonds in the char (Knicker et al., 2005). The FTIR spectra of E. occidentalis and of the char obtained at T = 967 K are reported in Figure 6.1 and confirm the modifications to the biomass chemistry when it was exposed to high temperatures. The spectra were baseline corrected, height normalized, and shifted for clarity.

In E. occidentalis spectrum, the region between 3100 and 3700 cm^{-1} contains signals because of the stretching vibration of O–H bonds due to the hydroxyl groups in phenolic and aliphatic structures (alcohol, phenol, amine, amide, and carboxylic acid groups) in both the holocellulose and lignin matrix. The next region in the spectra, between 2850 and 3050 cm^{-1}, contains signals due to the

stretching vibrations of C–H and CH_2 groups inside sugar rings and the stretching of CH_2 and CH_3 in aromatic methoxyl groups and in methyl and methylene groups of side chains in the lignin structure (Yang et al., 2007; Boeriu et al., 2004).

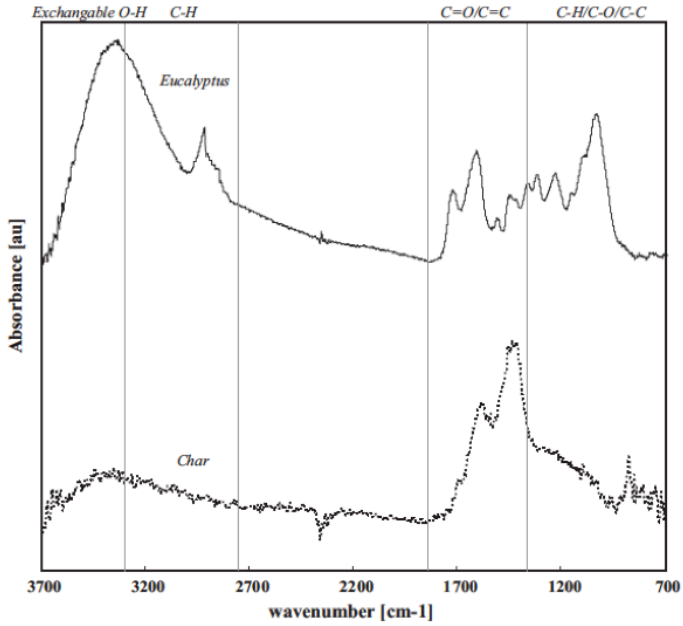

Figure 6.1: FTIR-spectra of E. occidentalis and of the corresponding char obtained at T = 967 K.

The last region, between 1800 and 700 cm^{-1}, contains overlapping signals of stretching and bending absorptions of many different functional groups (C=O of carbonyl and carboxylic groups, C–OH, C–H, C=C, and C–C). Signals below 700 cm^{-1} were not detected because the spectral range was cut by the ATR crystal (zinc selenide). The spectrum of the char sample was quite different from that of the parent feedstock. The shape of this spectrum indicates that the characteristics of the feedstock functional groups were completely absent. The char sample was characterized by a complex carbonaceous network with condensed aromatic moieties, as only signals from C-C and C=C bending modes were detected.

The proximate analysis results of the char, reported in 5.3, show that, at 688 K, the volatile content was still high and continued to decrease linearly up to 967 K; however, the opposite trend was observed for the carbon content up to 873 K. At higher temperatures, the presence of steam in the reaction environment induced carbon consumption, due to the onset of char oxidation reactions responsible for CO and CO_2 production, as reported in the figure of the gas

(Figure 5.2). At 967 K, agreeing with the increase in the O/C ratio, the content of fixed carbon decreased.
The HHV followed the same trend as the fixed carbon content did, so the highest value (28 MJ/kg) was obtained at T = 873 K; whereas ER in the char remained stable at approximately 40% up to 873 K and decreased to half at 967 K, due to the increase in the O/C ratio and the strong reduction in char yield. Though ash yield remained relatively unchanged at all the tested temperatures, its content increased from 8.4 to 16%, due to the reduction in volatile species up to 873 K and the consumption of fixed carbon at higher temperatures.

T, K	*pH*	*Na*		*Al*		*P*		*K*		*Ca*		*Fe*	
		C	*IR*	*C*	*IR*	*C*	*IR*	*C*	*IR*	*C*	*IR*	*C*	*IR*
		mg/kg	*g/g*	*mg/kg*	*g/g*	*mg/kg*	*g/g*	*mg/kg*	*g/g*	*mg/kg*	*g/g*	*mg/kg*	*g/g*
688	7.2	4437	0.15	196	0.06	2536	0.55	11745	0.76	18660	0.49	292	0.39
794	10.3	5600	0.15	235	0.06	3000	0.53	14500	0.77	23500	0.50	370	0.40
873	10	5721	0.14	309	0.08	3226	0.52	14665	0.71	24980	0.49	406	0.40
967	10	5760	0.09	384	0.06	3345	0.36	15145	0.49	23995	0.31	249	0.16

Table 6.2: Content (C) and ion recovery (IR) in the char obtained from pyrolysis of Eucalyptus at different final temperatures.

Table 6.2 reports the content of the main inorganic species in the solid residue (C) and the ion recovery in the char (IR). The ash composition analysis shows that it does not reproduce the composition of the corresponding parent biomass. Na and Al, which represent a great portion of E. occidentalis, as well as Fe were released at low temperature, thus indicating that these metal ions were bound to the organic matrix and released with the organic volatiles at temperatures below 688 K, causing a reduction in their concentration in the solid residue and low values for ion recovery in the char (Werkelin et al., 2010). On the contrary, a less pronounced release of K, Ca, and P was observed up to 688 K, thus resulting in the increase of their concentrations in the corresponding char and in higher values of ion recovery. K is the most thermally resistant, whereas Al is the most labile. At higher temperature, the recovery of all the examined inorganic species remained constant up to 873 K, indicating that no great devolatilization occurred. Nevertheless, due to the devolatilization of the organic matrix, the char was enriched with inorganics. At 967 K, the chemical modifications induced by the presence of steam in the reaction environment allowed for the release of both the inorganic and organic matrices, thus resulting in a decrease of ions recovery, though no substantial changes were observed for ions concentration in the solid residue. The concentration of alkali metals in the char at increasing temperature could be partly responsible for the increase in char pH. At 688 K, the pH was still neutral, probably due to the

presence of acidic groups in the char structure. At higher temperature, as observed in the literature for different biomasses (Luo et al., 2015), it is possible that a great reduction in acidic groups occurred. A decrease in the content of acidic groups and in the concentration of alkali metals in the char likely contributed to the increase in pH with increasing temperature.
The influence of temperature on char morphology was studied by adsorption tests of argon at 87 K and the adsorption isotherms are presented in Figure 6.2. The most striking feature of the argon isotherms is the presence of great ‘‘low-pressure hysteresis”, which is related to the entrapment of adsorbate molecules in very fine ultra-micropores with dimensions close to those of the adsorbate (Bailey et al., 1971), thus making the pore size distribution analysis difficult. Nevertheless, the shape of the isotherms gives some indications of char porosity.

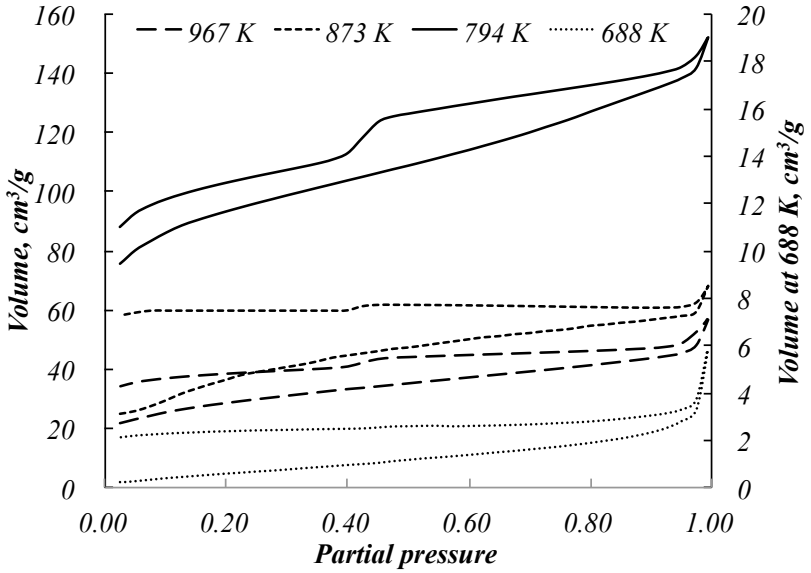

Figure 6.2: Adsorption isotherms of the E. occidentalis char at different pyrolysis temperatures.

The isotherm of char obtained at 688 K shows limited adsorption and is characteristic of a nonporous solid (type II isotherm).
The adsorption capacity of the char increased at 794 K and great uptake of argon occurred at very low relative pressures, indicating the presence of micropores. At this temperature, a type H4 ‘‘high pressure hysteresis” loop occurred indicating the presence of slit-like mesopores. At increasing temperature, the adsorption capacity of the char decreased as did the intensity of the ‘‘high pressure hysteresis”. Different from water uptake that depends on both char porosity and surface hydrophobicity (Gray et al., 2014), final argon uptake values account for the total porosity. This is consistent with the trend of

the BET surface for E. occidentalis char obtained at different temperatures (Figure 6.3).

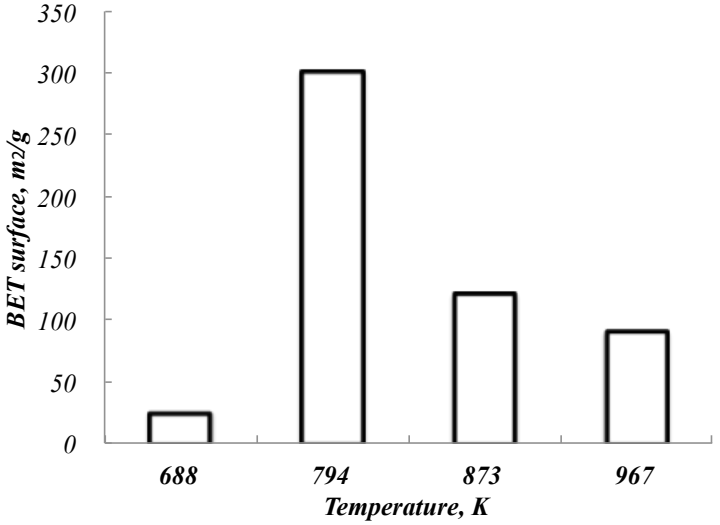

Figure 6.3: BET surface of the E. occidentalis char obtained from pyrolysis at different temperatures. The value of the E. occidentalis char at T = 688 K is multiplied by 10.

In agreement with the differences in argon uptake at very low relative pressures, the BET surface showed a non-monotonous trend with the temperature: the highest value, 300 m^2/g, was obtained at 794 K and it was greatly higher than the one obtained for the E. occidentalis char produced under nitrogen-assisted slow pyrolysis conditions (Martins et al., 2007). It is known from the literature that steam is able to perform a more efficient penetration of solid matter enhancing desorption, distillation and removal of volatiles (Minkova et al., 2001). On the contrary, during pyrolysis under a flow of nitrogen, higher char yields are obtained with lower porosity, due to the deposition of carbonaceous material inside the char pores (Minkova et al., 2001). At low heating rates, biomass structure is preserved during thermal treatment and the pore development and internal surface area are strictly correlated to the degree of devolatilization and to the formation of cracks inside the char matrix. Up to 688 K, the removal of a great amount of volatile matter created sparse void volume regions giving rise to a macroporous structure characterized by a low BET surface value. At higher temperatures, up to 794 K, the formation of cracks in the material caused micropores and mesopores regions to develop, leading to a great increase in surface area and porosity (Lehmann and Joseph, 2009). At high temperatures, structural ordering and micropore coalescence led to lower values of surface area (Lehmann and Joseph, 2009).

6.2 Influence of feedstock

Chars obtained from different feedstocks at T= 873K were compared. Table 6.3 shows the change in the atomic ratios of H/C and O/C from biomass precursors to the corresponding chars, char- acterization of char in terms of proximate analysis, HHV, and ER. In all the char samples, the atomic ratios of O/C and H/C were greatly lower than they were in the corresponding biomass precursor. In particular, for P. nigra the high extent of devolatilization was con- sidered responsible for the lowest O/C ratio in the produced char (0.07). S. alba char, containing the lowest amount of C and the highest amount of O, was characterized by the highest O/C atomic ratio (0.11). For all the produced char, H/C was in the range of anthracite, whereas the O/C ratio was in the range of coal (van Loo and Koppejan, 2007). Based on these results, all the produced chars had a high degree of aromaticity and maturation (Spokas, 2010); though, among them, P. nigra char would be more stable and have the highest potential for application in soil to sequester C for long periods.

Biomass	*O/C*		*H/C*		*HHV*	*ER*	*volatiles*	*fixed carbon*	*ash*
	Precursor	*Char*	*Precursor*	*Char*	*MJ/kg*	*%*	*wt % dry basis*		
P	0.69	0.07	1.39	0.33	28.6	31.8	20.1	67.2	12.8
S	0.68	0.11	1.36	0.29	24.0	35.5	19.5	59.2	21.3
F	0.71	0.10	1.43	0.28	26.2	33.0	28.7	56.7	14.6
E	0.72	0.09	1.38	0.29	28.0	42.5	24.3	64.3	11.4
AD	0.73	0.10	1.46	0.43	25.4	33.2	18.1	59.9	22.0

Table 6.3: Composition and properties of char obtained from different biomasses at T = 873 K.

The O/C ratio was close to the value obtained for cellulose char under the same operating conditions as those used for this study (Ragucci et al., 2013). This result can be explained considering that cellulose is the most abundant component in most of the vegetal biomasses and contributes more than the other organic components to the devolatilization of oxygenated compounds leaving a solid residue with very low O content. The analysis of the content of extractives, hemicellulose, and lignin, confirmed that the cellulose content was highest for P. nigra (57 wt% daf basis) and lowest for S. alba (30 wt% daf basis) and that an increase in cellulose content corresponded to a decrease in O/C ratio in the pyrolyzed sample.

The O/C ratio and ash content of the char are fundamental in determining its HHV: S. alba char had the lowest HHV followed by the F. oxyphylla and A. donax chars, whereas the P. nigra and E. occidentalis chars had the highest energetic content. Nevertheless, if one considers the ER value for char, E.

occidentalis is the best choice, as it reached an ER value of 42.5%; whereas a greatly lower value (31.8%) was obtained for the P. nigra char.
The volatile content of char was quite high for F. oxyphylla (28.7%), whereas the lowest values where derived from P. nigra (20.1%) and S. alba (19.5%). Intermediate values where observed for the E. occidentalis char. The highest was the volatile content, the lowest is the fixed carbon content. The S. alba and A. donax chars, due to their high ash content, did not share this correlation. These results reveal that E. occidentalis char is the best choice for energy applications, given it had the highest HHV and ER and the lowest ash content.

Biomass	*pH*	*Na*		*Al*		*P*		*K*		*Ca*		*Fe*	
		C *mg/kg*	*IR* *g/g*	*C* *mg/kg*	*IR* *g/g*	*C* *mg/kg*	*IR* *g/g*	*C* *mg/kg*	*IR* *g/g*	*C* *mg/kg*	*IR* *g/g*	*C* *mg/kg*	*IR* *g/g*
P	10.1	627	0.05	192	0.04	3070	0.56	12010	0.71	27915	0.68	219	0.15
S	9.9	1061	0.08	4062	0.17	5249	0.76	20980	0.71	34080	0.72	2406	0.66
F	10	1008	0.06	149	0.03	6610	0.99	28180	0.94	28030	0.97	157	0.13
E	10	5571	0.14	187	0.05	3390	0.55	14320	0.70	25100	0.49	406	0.40
AD	10	652	1.73	192	0.42	2309	0.82	40825	0.88	3539	0.81	331	0.67

Table 6.4: Content (C) and ion recovery (IR) in the char obtained at T = 873 K from different biomasses.

Table 6.4 reports the content of the main inorganic species in the chars from the different biomasses expressed both as mass of inorganics per mass unit of char (C) and as recovery of the inorganic ion in the char with respect to the corresponding content in the raw biomass (IR). The ash contents in the char agreed with their contents in the corresponding precursors, with the highest amounts in the A. donax and S. alba chars at 22 and 21.3%, respectively. The main components of the char ash were P, K, and Ca, for all the tested biomasses, all of whose concentrations increased after thermal treatment. As already observed for E. occidentalis, the thermal treatment led to a great devolatilization of Na and Al, resulting in lower concentrations of these elements in the corresponding chars and in low values of ion recovery. The high value of Na ion recovery measured for A. donax char (three reliable replicates were done for both the biomass and char samples) may be due to the stability of this ion in the raw biomass. In agreement with the results obtained for the E. occidentalis char P, K, and Ca were the most thermally resistant inorganics in all the tested biomasses, whereas Na and Al were the most labile and Fe was present in recalcitrant forms only in the S. alba and A. donax chars. Chars from the other biomasses also had an alkaline nature and negligible differences occurred among them. The high presence of exchangeable cations (Na, K, and Ca) as well as the consequent alkalinity allows this char to be considered for application in the agronomic field as a source of nutrients. If one considers the

overall content of these cations, S. alba and F. oxyphylla chars are the most appealing as a source of nutrients. Nevertheless, if the supply of a specific element is needed, the E. occidentalis and A. donax chars are preferred as they could provide an important source of Na and K, respectively. The adsorption isotherms of the different chars were studied by adsorption tests of argon at 87 K and the adsorption isotherms are presented in Figure 6.4. The adsorption isotherms of the different chars were very similar to the one obtained for E. occidentalis char at T = 873 K. Except for the P. nigra char, a small Argon uptake was concentrated in the low-pressure range, whereas in the high-pressure range further adsorption was observed, up to a steep increase at a relative pressure close to 1.

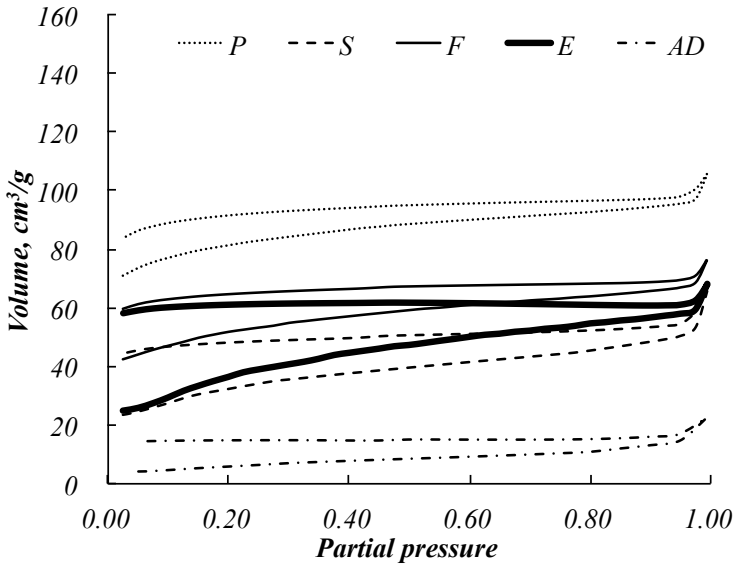

Figure 6.4: Adsorption isotherms of chars obtained from pyrolysis at T = 873 K of different feedstocks.

These Type II isotherms are associated with narrow slit pores including pores in the micropore region.

A correlation was observed between the BET surface area of the different chars and the cellulose content of the parent feedstock. This is in agreement with the role of cellulose in determining char porosity (Giudicianni et al., 2013) in that the BET surface was very high for the P. nigra char, whose cellulose content was 55.3 wt% dry basis (db), whereas lower but increasing values were observed for the A. donax, S. alba, E. occidentalis, and F. oxyphylla chars containing 40.5, 28.1, 40.8 and 43.7 wt% db, respectively. Except for the A. donax, the BET surface seemed to correlate proportionally with cellulose content. As already observed for the E. occidentalis char, the BET surface of

the P. nigra char obtained under a steam atmosphere was higher than the values reported in the literature for the same biomass processed under similar thermal conditions in a nitrogen atmosphere, whereas a similar value of BET surface was obtained by Zheng et al. (2013) for A. donax char obtained under nitrogen-assisted slow pyrolysis conditions.

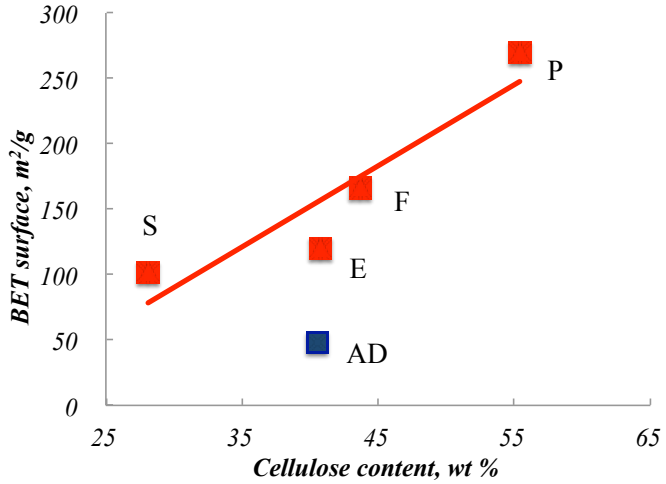

Figure 6.5. Correlation Cellulose content and BET surface for all chars.

It is well known that high values of BET surface assume a relevant role in applications requiring high sorption capacity (e.g. removal of undesired elements from fluid streams). More specifically chars with values of BET > 400 m^2/g are generally considered good sorbents (Downie et al., 2009; Keiluweit et al., 2010). In addition, high values of BET surface could be important also in the application of char for the production of bio-composites, as the char's matrix could allow for proper blending of the natural fiber and the molten polymer (Srinivasan et al., 2015). Based on the results obtained in the present study, among the chars produced at T = 873 K, P. nigra char has the highest potential to be used effectively in these applications. Nevertheless, E. occidentalis char produced at T = 794 K gives even higher valued than P. nigra char. At low temperature char porosity is mainly determined from the void volume left from the volatiles released by the biomass during the heat treatment (Lua et al., 2004). The devolatilization of cellulose, the main responsible of the release of volatiles during biomass pyrolysis, can be considered completed at temperature lower than 873 K (Giudicianni et al., 2013), thus suggesting to explore lower temperatures also for P. nigra, given its high cellulose content.

7. Results and discussion: biomasses from contaminated solis

The topic of this section is the results of tests about the pyrolysis of the biomasses from phytoremdiation.
Except the final temperatures, the pyrolysis tests were performed on the different parts of Populus nigra (P. nigra) and Arundo donax (A. donax) in the same conditions of non-contaminated biomasses (HR_{sp}= 4 K/min, P= 5*105 Pa).
The choice of the final temperature has been made step-by-step, on the basis of the results of PTEs concentration in the several chars. Indeed, it should be reached a compromise between the maximization of the PTEs in the char and better features for other possible applications.
According to the different part of the plants we used a different range of temperature: the poplar branches (617-873 K), leaves (653-873 K), rhizomes and culms (703-873 K). The content of the most quantity heavy metal has been monitored in each selected plant part. In particular we measured the Cd and Pb for P. nigra's branches, instead Cd, Cu, Pb and Zn from leaves. The content of Cd, Pb and Zn were detected for chars produced from both parts of the A. donax.
In this chapter is reported the study conducted for all feedstocks about both sections: reporting the product yields and the releasing rate of the main gaseous species (CO, CO_2, CH_4 and H_2).

7.1 Slow pyrolysis of Populus nigra: products yields and characterization

The yields of products obtained from each pyrolysis experiment on branches and leaves of P. nigra, are shown in Figure 7.1. An increase of pyrolysis temperature led to a decrease in the yields of char for both feedstocks and the effects could be due to the greater primary decomposition or through secondary decomposition of char residues. The highest yields of char were obtained at low temperatures, namely T= 613 K and T= 653 K, it indicates that the material has been only partially pyrolyzed (Katyal et al., 2003). Mainly the degradation depends on the content of the main components in the raw materials, but the different amount of ash and inorganics may also affect the results. The branches were characterized by high amount of ash, especially K content than leaves as showed in the Table 5.2 (K content in branches was 4477 ppm; K in leaves 3569 ppm).

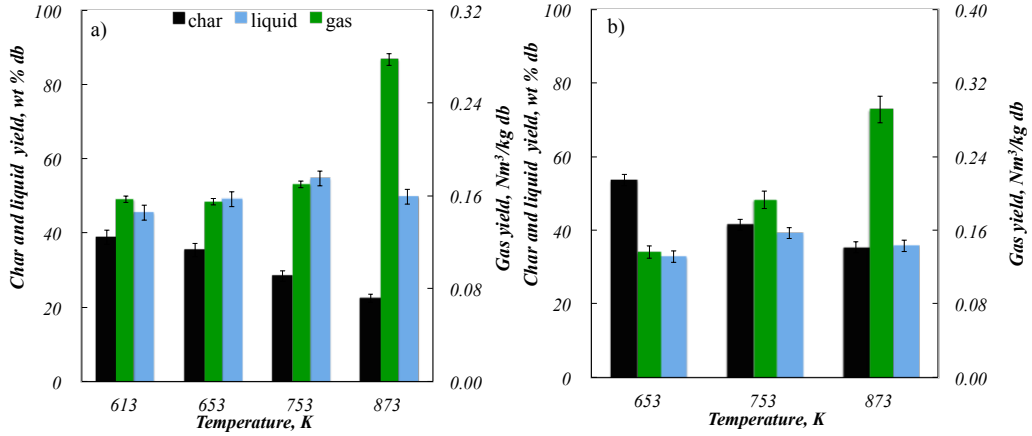

Figure 7.1. Yields of pyrolysis products of branches: (a) and leaves (b) at different temperatures.

In the branches case, the char yield decreases from 38.8% to 35.40%. Where the char yield reaches 22.45% we had the highest weight loss in the range of 753 K to 873 K. The decreasing yield of the char was shown an increase of liquid that was the highest at 753 K with 49.8 %.

The same trend was observed for the leaves in which the char was attested higher than the results of the branches in whole temperature range. Higher temperature led to the loss of char with an increasing of gas production. Nevertheless, for both case, till the temperature of 753 K, the gas yield was on average constant, it increased considerably in range of 753-873 K.

At 653 K, regard the leaves, the highest yield was the char one compared with the gas and liquid yield, in opposite to the result on the other part plant. Whereas, by the increasing of the temperature the highest yield was the gas

ones. The char and liquid yields pointed out the differences *in betwe*en leaves and branches. Considering the entire temperature range: the char yield of the leaves was more than the branches ones, which they produced more liquid. Those detected differences were related to the ashes content and organic fraction of the raw materials. The leaves ashes content was more than branches, respectively with 16.4% and 1.9%, and which explained the most char yield of them. Instead, at low temperature, we detected the lowest liquid and gas yield because of minor content of organic fraction in the leaves. It should be noted that at intermediate temperature as 753 K, the increasing of the both yields were correlated to the inorganic species. Particularly, the secondary decomposition reactions of liquids, still trapped in the solid organic matrix, at higher temperature were released due to the catalytic actions of the inorganic fractions.

In the Figure 7.2 is represented the releasing rate of CO, CO_2, CH_4 and H_2 for branches and leaves. The release of CO_2 from branches started at around 420 K. There are two peaks of CO_2 and the release was detected at 670 K and 775 K.

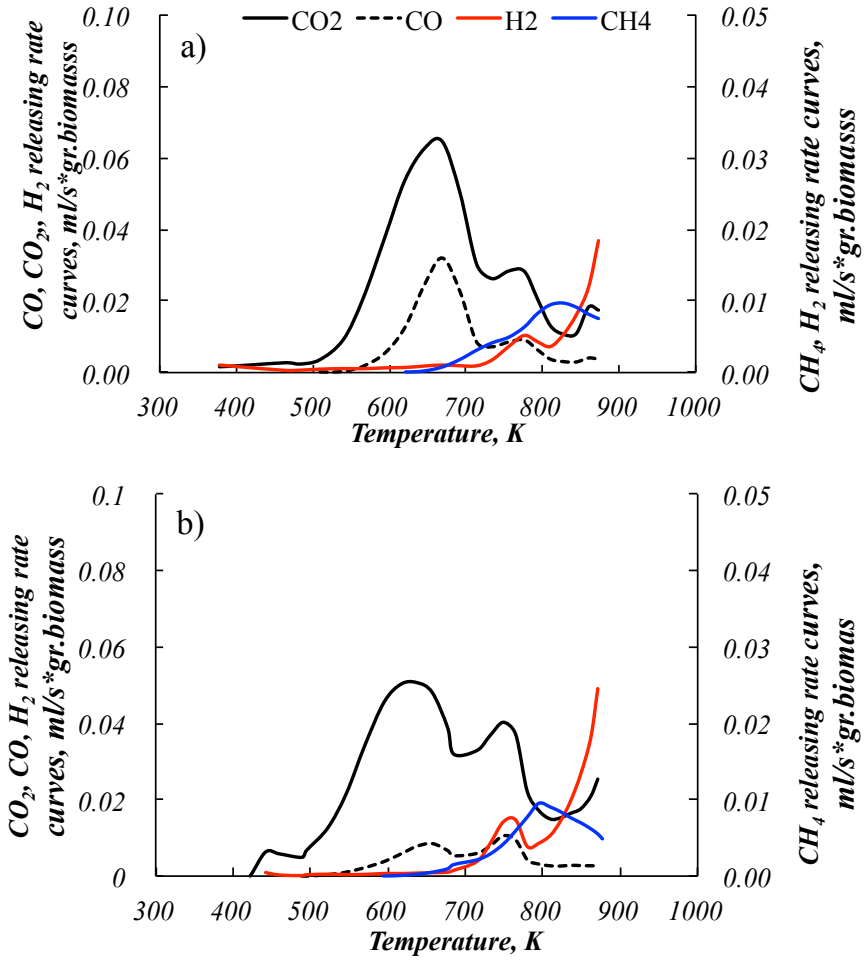

Figure 7.2. Releasing rate (ml s -1 g -1 biomass on daf basis at STP conditions) of CO, CO2, CH4, and H2 for branches and leaves as a function of temperature.

They can be assigned respectively to the decarboxylation of the carboxylic acids from holocellulosic fraction, and also to the cracking of primary pyrolysis products at higher temperatures. The same reactions were observed for the release of CO_2 from leaves, even though the temperatures of the peaks are about 30 K lower than the previous case. Which could be explain to the higher content of alkali and earth alkali metals in the leaves more than in the branches (for leaves Na is 573, K is 3596 and Mg 2325, Ca 37500 ppm; for branches Na is 206, K 4477, Mg 836 and Ca 9407 ppm). These metals are known to catalyse the decomposition of holocellulose.

The releasing rate of CO along the line of the temperature was similar for branches and leaves and qualitatively followed the ones of CO_2. Instead we had

two distinct peaks: for branches at 670 and 775 K while for the leaves at 640 and 645 K.
These peaks could be explained respectively by the onset of the decarbonilation reactions and by the breakdown of primary pyrolysis products at a higher temperature (Lievens et al., 2009). At 630 K CH_4 and H_2 were detected in the gas phase. By comparing the formation of CH_4 and H_2 in the case of leaves, the peaks of the release were anticipated of 30 K. At the same temperature range of CH_4 release, even C_2H_4 and C_2H_6 (not reported in the figure) were released in smaller amounts.
Table 7.1 reports the gas composition and HHV.

branches							
T, *K*	CO_2	CO	CH_4	H_2	C_2H_4	C_2H_6	HHV
			wt%				*MJ/Kg*
613	73.6	25.8	0.5	0.1	0.0	0.0	3.1
653	76.0	22.6	1.0	0.2	0.1	0.2	3.2
753	79.0	17.3	2.4	0.4	0.3	0.6	4.1
873	75.4	16.4	4.4	2.7	0.3	0.8	8.5

leaves							
T, *K*	CO_2	CO	CH_4	H_2	C_2H_4	C_2H_6	HHV
			wt%				*MJ/Kg*
653	89.8	9.5	0.5	0.2	0.0	0.0	1.5
753	87.2	8.7	2.1	0.5	0.4	1.0	3.5
873	85.3	7.4	3.6	2.4	0.4	0.9	6.8

Table 7.1: Composition and HHV of the gaseous product from pyrolysis of branches and leaves at different temperatures.

If we compared the different parts of the plants, it pointed out than the leaves produced more CO_2, around the 10% more than the branches. Above mentioned concentration was slightly reduced with the increasing of the temperature, instead about the branches the CO_2 increased up to 753 K. Meanwhile, the branches released above all CO, and in both ones, it decreases with high temperature. If we considered the methane and hydrogen, there weren't any difference in between the elements of the plant up to 753 K, over that temperature, the branches produced more CH_4 (4.4 wt %) and H_2 (2.7 wt %). The HHV, calculated taking into account the concentration of each species, the highest value was obtained at 873 K in branches case.

7.2 Slow pyrolysis of Arundo donax: products yields and characterization

In the Figure 7.3 are illustrated the pyrolysis product yields of rhizomes and culms.

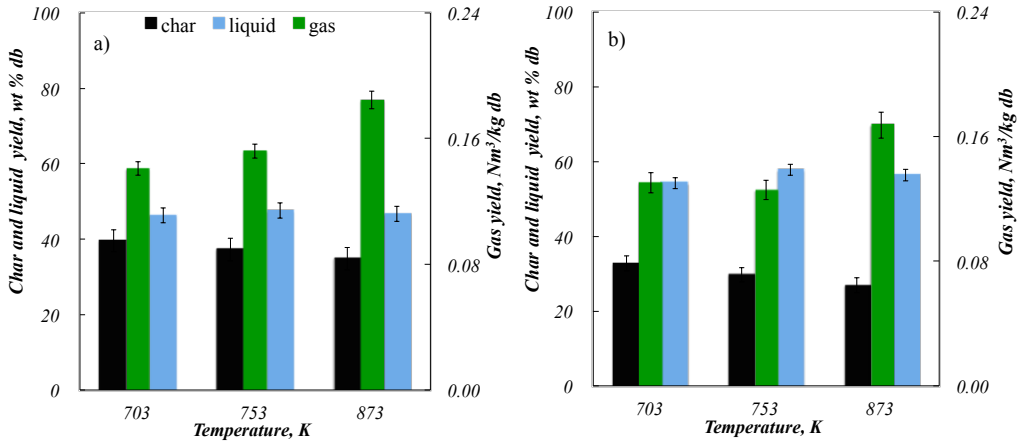

Figure 7.3: Yields of pyrolysis products of rhizomes (a) and culms (b) at different temperatures.

In the temperature range 703-873 K, the char yield for both parts of A. donax slightly decreased with the increasing of temperature, whereas the liquid yield was almost constant. Even if the culms produced more liquid, in whole temperature range the char yield was lower compared to the rhizomes, as well as the gas yield. At 703 K, the rhizomes char yield was 39 % compared to the 32.75 % of the culms.
Contrary to the highlighted in the case of P. nigra, the difference on the char yields of the two parts of A. donax, was not related to the ash content in the feedstock.
Both organs of the plants were characterized by the equal ash content (rizhomes with 1.1 % and culms 0.9). These results could be a consequence of the organic composition of the plants. As reported in the results of proximate analysis, the rizhomes were characterized by a low volatiles fraction but higher fixed carbon content than the culms.

In the Figure 7.4 the releasing rate of CO, CO_2, CH_4 and H_2 for branches and leaves is represented.
The release of CO_2 started around at 470 K with a maximum at 620 K from rhizomes, and at 610 K for culms. The same evolution was not observed for the release of CO, that it started around at 510 K for rhizomes and 530 K for culms, with the peaks at 640 K for both part of the plants. There were no different behaviours for the A. donax. The different parts were characterised by the same

temperature of the release for the CH_4 starting at around 780 K. The releasing rate of CH_4 and H_2 along the line of the temperature was qualitatively similar. Table 7.2 shows the composition of the gas mixture and the corresponding HHV for each pyrolysis temperature.

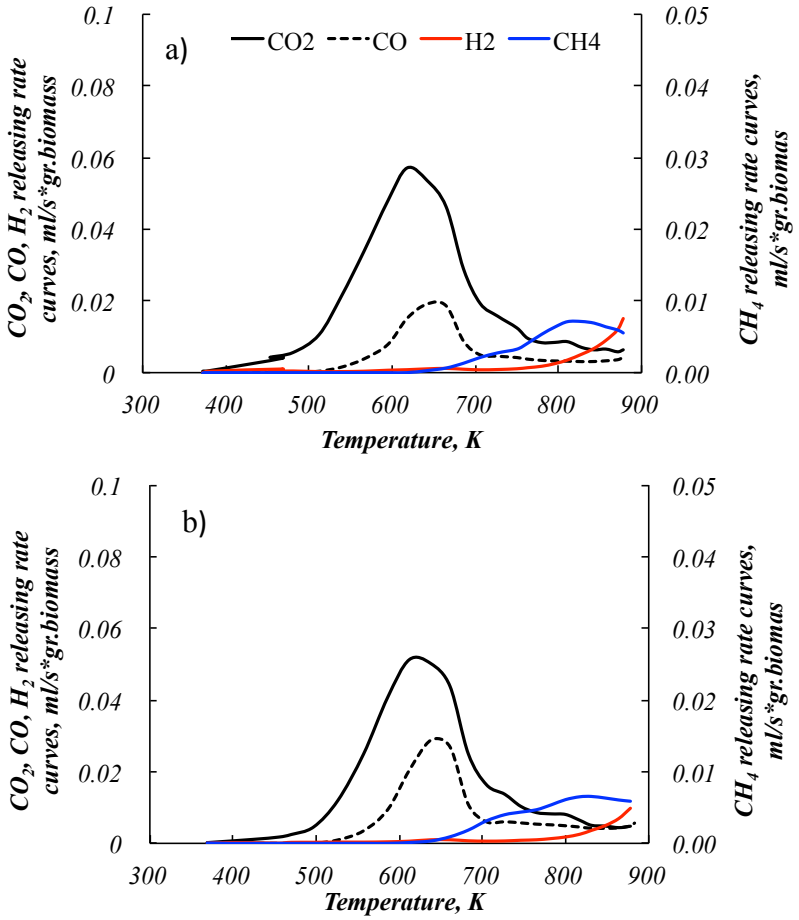

Figure 7.4: Releasing rate (ml s -1 g -1 biomass on daf basis at STP conditions) of CO, CO2, CH4, and H2 for rhizomes (a) and clums (b) as a function of temperature.

Even as reported in the Table 7.2, was not observed a difference between the two plant parts in the composition of the gas mixture in the range of 703-753 K. The most significant variations can be observed from 753 to 873 K with the increasing of the concentration of all species, at the expense of CO. At 873 K the CO_2 concentration was the lowest, and the CO ones reached its maximum.

rhizomes							
T, *K*	CO_2	CO	CH_4	H_2	C_2H_4	C_2H_6	HHV
			wt%				*MJ/Kg*
703	84.6	12.9	1.5	0.2	0.2	0.6	2.8
753	83.67	12.8	2.2	0.2	0.3	0.8	3.3
873	78.8	14.3	4.7	0.9	0.4	0.9	6.0

culms							
T, *K*	CO_2	CO	CH_4	H_2	C_2H_4	C_2H_6	HHV
			wt%				*MJ/Kg*
703	77.6	19.7	1.8	0.1	0.3	0.5	3.5
753	77.8	19.8	1.6	0.1	0.2	0.5	3.4
873	71.6	21.1	5.2	0.8	0.4	0.8	6.7

Table 7.2: Composition and HHV of the gaseous product from pyrolysis of rhizomes and culms at different final temperatures

Comparing the two parts, it was noted that for all temperature range the CO_2 concentration was higher in rhizomes than in culms. For the CO, the opposite trend was observed, which its highest production was observed at 873 K for culms.

At highest temperature, the development of H_2 and C_2H_4 and of C_2H_6, has reached the same values, in both feedstock. Their concentration has been always <1%. HHV values increased from 2.8 to 6.00 MJ/kg for rhizomes and from 3.5 to 6.7 MJ/kg for culms. Comparing the results of the A. donax with the obtained from P. nigra were noted common trends.

The results of the branches of P. nigra were very similar to results of the culms. These organs of the plants were characterized by a less concentration of CO_2 and higher CO. Observing the results of the leaves and rhizomes the correlation was similar, with an opposite trend, namely a higher CO_2 production than CO. consequently the low values of HHV were obtained for leaves and culms.

Based on the comparing of gaseous species we pointed out a correlation among the structural organs of the plants, even if they were by different nature: lignocellulosic and the herbaceous.

8. Char characterization

8.1 PTEs (Cd, Pb, Zn and Cu) investigation

The aim of the study on contaminated biomass regards the identification of pyrolysis temperature suitable for the maximization of PTEs in the solid. In this section, is presented the discussion on the PTEs evolution during the pyrolysis. On the basis of ICP/MS analysis performed on all chars, it was possible to represent: Cadmium, Lead, Zinc and Copper concentration is illustrated as a function of temperature; the Ion Recovery in the chars. The metal concentration is intended as mass of ion per mass of char and it is used to calculate the Ion Recovery obtained multiplying it by char yield and dividing by the mass of ion in the raw biomass. The heavy metals concentration and the corresponding Ion Recovery for the different organs of the P. nigra and A. donax are compared.

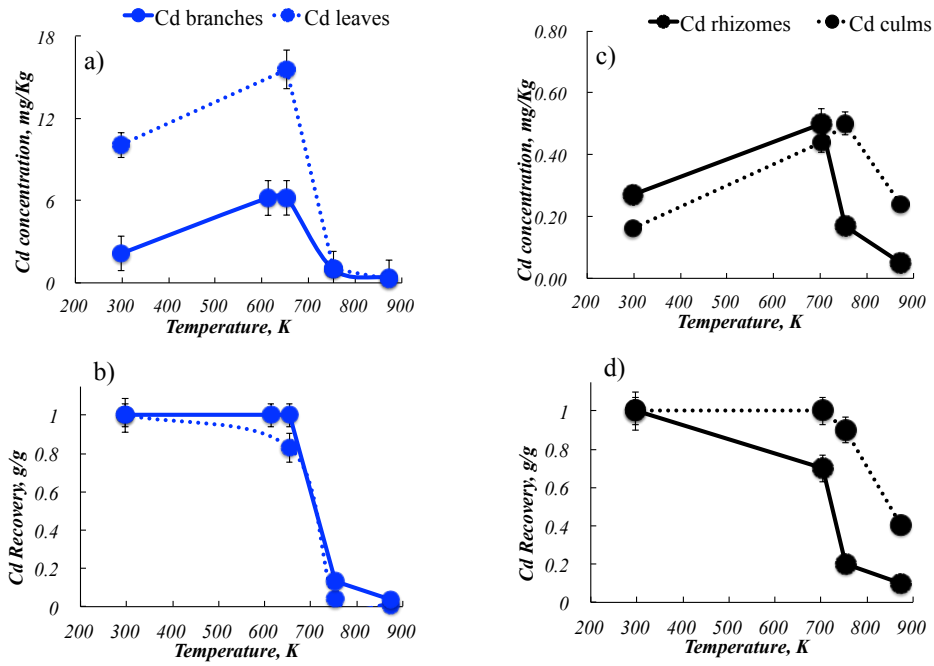

Figure 8.1: Concentration (a and c) and Ion Recovery (b and d) of Cd in the chars: P. nigra (branches and leaves) and A. donax (rhizomes and culms) at different final temperatures.

The concentration of Cadmium in both organs of the poplar was maximum at 653 K, over such temperature the Cd Recovery was started to decrease slightly. At this temperature, Cd Ion Recovery (panel "b") slightly decreases and the organic matrix of the original feedstock strongly loses weight resulting in char yields equal to 35.4 and 53.6 wt% for branches and leaves, respectively. This was determined the increase of Cd concentration in the char produced at 653 K.

In both cases, increasing the temperature, the Ion Recovery decreased rapidly. This was due to a release of the metal in the gas phase. In agreement with the experimental results of literature, obtained under nitrogen assisted pyrolysis in the temperature range 623-723 K (Bert et al., 2017; Stals et al., 2010a). At the same time, the decrease of char yield was slighter thus determining the decrease of Cd concentration in the solid residue.
As reported by Lievens et al. (2008b), the degree of cadmium volatilization increases with the temperature. In their experiments performed in the temperature range 623-873 K on sunflower and birch the biomasses were mixed with sand and fumed silica. Even though they were operated in fast pyrolysis conditions, the behaviour of Cd was qualitatively similar. At 673 K, the Cd retained in the solid was 82%, whereas it decreases at 52% and 11% at 773 K and 873 respectively. In this study at 753 K, Cd recovery in the char is much lower, about 10%. This aspect confirms that the results obtained by Lievens were affected by the presence of silicates in the sand and in the fumed silica responsible for adsorbing Cd and to react with it to form more stable compounds.
Cd trend was studied also on Arundo donax in order to highlight a possible interaction with the biochemical composition of the feedstock.
The first temperature selected for the studies of the A. donax was 703 K. The initial content of the Cd in the two organs of the A. donax was lower than the one present in the P. nigra.
As reported in the panel “c”, the behaviour of Cd in the A. donax was similar to the P. nigra, except for culms, where Cd is more resilient to the temperature increase. At 753 K, the devolatilization of the Cd was not completed and the Ion recovery was still about 40% at 873 K.
Probably, Cd devolatilization strongly depends on the pyrolysis conditions, but also on the chemical form in which it is present in the specific part of the plant. Furthermore, we have to consider in which the main components, were bounded the metals.
Even if, the A. donax was classified in the category of a herbaceous species, the lignin content was higher than the in the P. nigra, as reported in section 4, Table 4.1. The content of lignin in A. donax was 19.7 % and in P. nigra 11.6 %. It is well known that lignin is the component of the plant that devolatilizer slowly in a wide temperature range. It is possible that in the case of culms Cd still retained in the char at 873 K belongs to the lignin matrix that slowly devolatilizer. On the contrary, in the P. nigra and in the Arundo rhizomes the Cd trend is more comparable to the devolatilization/decomposition of a mineral compound that occurs at a specific temperature.

In the case of lead, for each feedstock different performances were obtained. Observing the Figure 8.2 it can be seen that Pb slowly was concentrated in the chars when the pyrolysis was conducted up to 653K.
In the temperature range, 653-753 K the concentration of Pb in branches and leaves rapidly increase respect to the consecutive range 753-873 K.
Conversely to the P. nigra, high accumulation of Pb in the chars was evidenced already at low temperature in both parts of A.donax.
This opposite accumulation of Pb in P. nigra and A.donax was not confirmed when the Ion Recovery was employed. As reported in panel "b" and "d", the devolatilization slightly was appeared in the leaves, whereas it was still negligible in the branches and in the parts of A. donax.

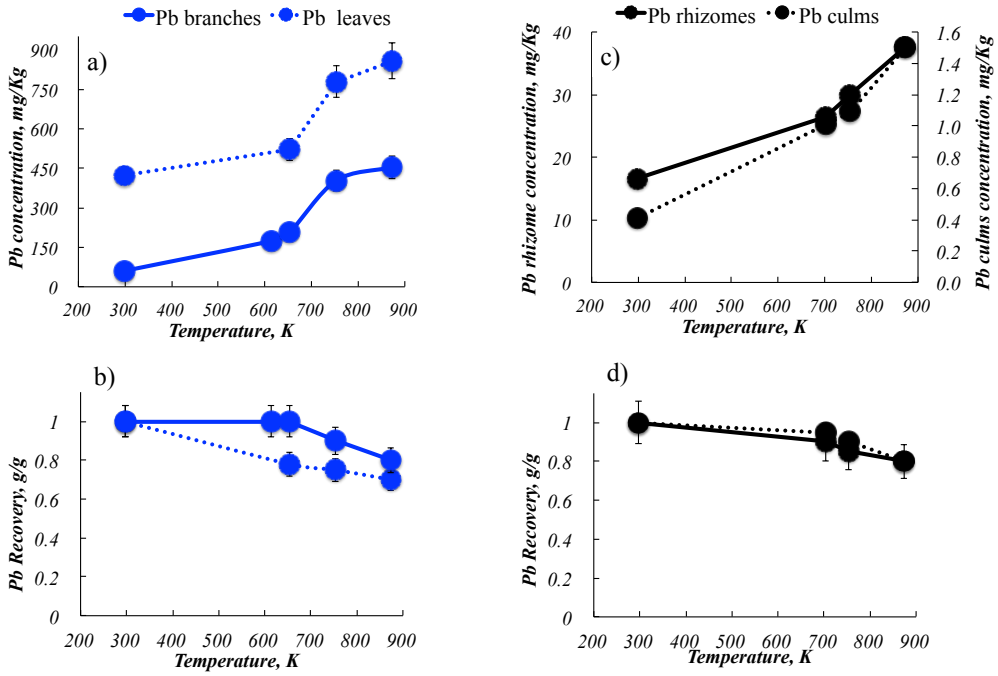

Figure 8.2: Concentration (a and c) and Ion Recovery (b and d) of Pb in the chars: P. nigra (branches and leaves) and A. donax (rhizomes and culms) at different final temperatures.

The devolatilization starts slightly at 753 K in the Populus leaves, whereas it is still negligible in the branches and in the parts of A. donax. Contrary to what observed for Cd, devolatilization proceeds slowly up to 873 K. At this temperature, Pb recovery was still significant for both biomasses, about 80% at 873 K and no relevant differences were observed for the different parts of the plants. Therefore, the difference in Pb concentration at higher temperature was due to the devolatilization of the organic fractions, as explained for Cd. The

char yields of branches and leaves were decreased of 6 % in the range 753-873 K. On the contrary, for rhizomes and culms 2.5 % of yield decrease is observed. Instead, for rhizomes and culms, 2.5 % of yield decrease was observed. This determined a steep increase of Pb concentration in the char from 753 to 873 K for A. donax.

Copper and Zinc behave similarly to Pb. Their concentrations and the corresponding Ion Recovery, as a function of temperature are illustrated in Figure 8.3 and Figure 8.4.

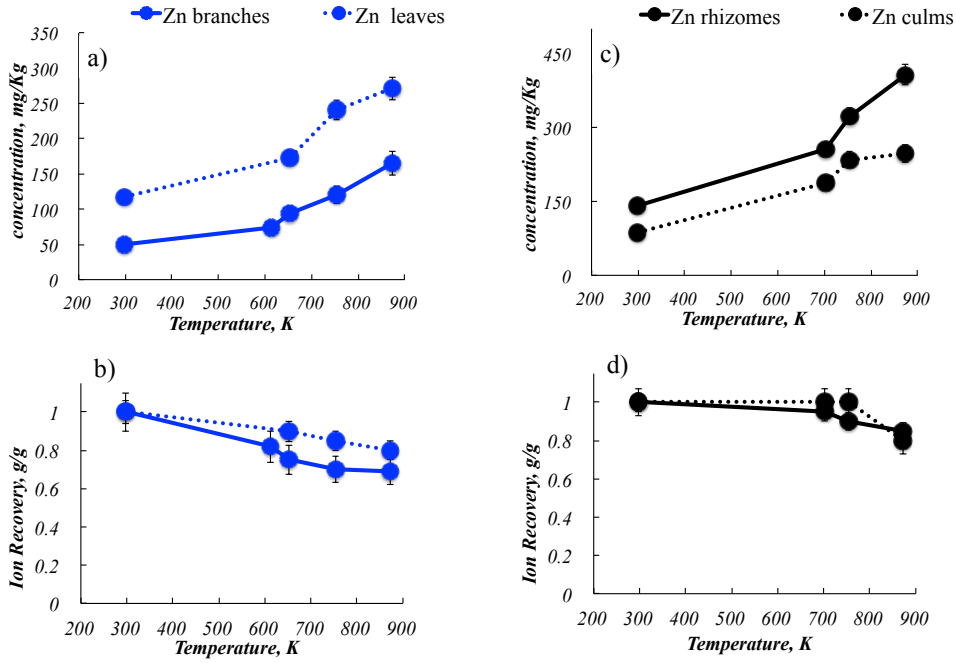

Figure 8.3: Concentration (a and c) and Ion Recovery (b and d) of Zn in the chars: P. nigra (leaves) and Zn in the chars from A. donax (rhizomes and culms) at different final temperatures.

As expected, the measured metal contents in the char were strongly enhanced compared with the initial precursors.

It should be noted that in a both Figure, Cu and Zn concentrations were characterized by the same trend in leaves case, as well as the corresponding Ion recovery. The concentration of the two metals was increased in the Populus leaves, because of the great devolatilization of the organic matrix with respect to the ones of the metals that were less relevant and slow. As for Pb, the zinc was more stable in Arundo rhizomes and culms since its devolatilization was started at the temperature higher than 753 K, even though at 873 K the recovery of Zn was about 80% in all the chars.

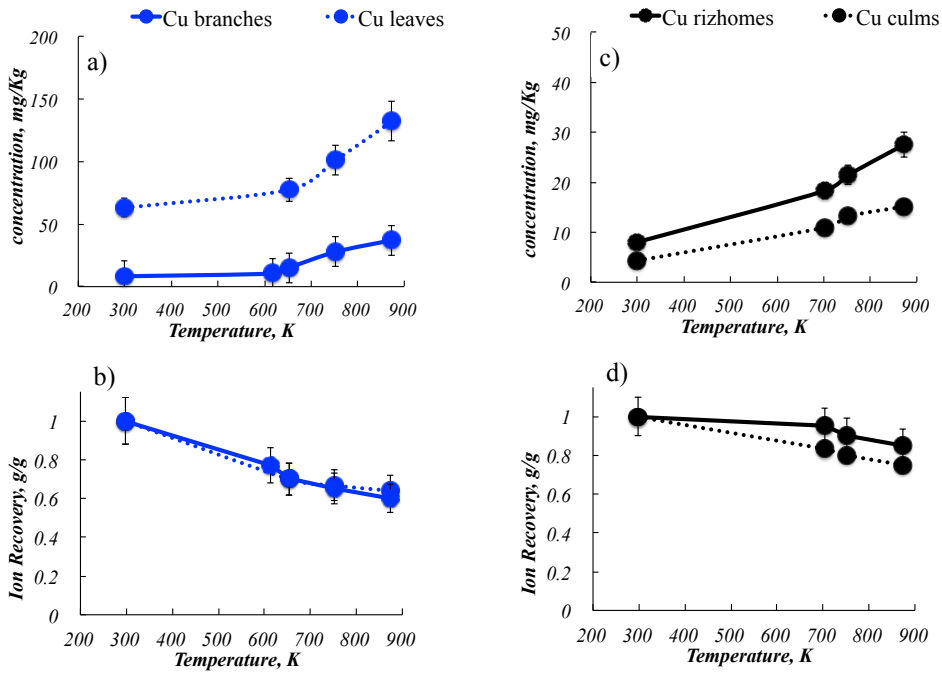

Figure 8.4: Concentration (a and c) and Ion Recovery (b and d) of Cu and Zn in the chars: P. nigra (leaves) and Zn in the chars from A. donax (rhizomes and culms) at different final temperatures.

The Pb and Zn results, were in agreement with the ones conducted on a contaminated soil mixed with woody biomass, reported in the studies of Debela (2012). In this experiment, the Pb and Zn remain immobilized in the char obtained from pyrolysis conducted at 673 K. Other studies (Ozkan et al., 2016), confirmed the stability of Zn in the solid residue obtained from the pyrolysis of sunflower, corn, rape and willow stems and leaves, conducted in N_2 in a fixed bed reactor, at the final temperature of 623 K and 723 K.

The devolatilization of Cd, Cu, Zn and Pb under elemental forms is unlikely in the selected temperature range, if the corresponding temperature of the boiling-points is considered (Cd: 767 °C 1040 K; Zn: 907°C 1180 K; Pb: 2022 K). Metals may be present under associated forms with, for instance, chlorides to form volatiles complexes. Literature findings obtained in the oxidizing atmosphere (Ju et al., 2013; Abanades et al., 2002) suggests that when Cd is associated with chlorine its devolatilization in gas phase occurs at temperatures lower than the ones typical of metal oxides devolatilization. However, the results obtained in the present work show that Cd containing compounds are even more volatile than the chlorides. Moreover, the Cl_2 content available in the feedstock to form $CdCl_2$ (branches 58 ppm, leaves 39 ppm, rhizomes 111 ppm and culms 87 ppm) is quite low with respect to the total amount of metals (K, Na, Mg, Cd) that could easily be linked to chlorine.

8.2 Ash composition: K and P investigation

Many studies were reported the effectiveness of biochar in improving soil quality and crop production (Lehmann et al., 2006; Liang et al., 2006; Laird, 2008; Atkinson et al., 2010; Van Zwieten et al., 2010; Rajkovich et al., 2011; Ippolito et al., 2012; Spokas et al., 2012; Liu et al., 2013). The positive impact of biochar could be due to a range of potential reactions that remove soil-related constraints otherwise limiting plant growth: soil nutrient status and soil pH, toxins, improved soil physical properties and improved N-fertilizer use efficiency (Chan & Xu, 2009; Van Zwietenet al., 2010). As biochar was produced by pyrolysis of biomass it often contains a high varying amounts of plant macronutrients (phosphorus (P), potassium (K), magnesium (Mg), calcium (Ca) etc.) and micronutrients (iron (Fe), sodium (Na) (Chan & Xu, 2009; Lehmann et al., 2011).
In Table 8.1 is reported the content of the elements of interest, for all chars. They can be retained in the chars produced during pyrolysis, affecting their chemical properties and conditioning the valorisation routes (Dias et al.2017).

Ash composition

Populus nigra

	branches				**leaves**		
T, K	**613**	**653**	**753**	**873**	**653**	**753**	**873**
	mg/kg db						
Na	414 (38)	882 (<1)	351 (4)	634 (24)	1223 (3)	1912 (0.2)	2023 (9)
Al	273 (95)	179 (5)	448 (14)	507 (6)	2081 (8)	2582 (3)	4654 (1)
P	885 (<1)	974 (4)	1822 (2)	3074 (<1)	1899 (3)	2300 (1.4)	2614 (9)
K	8728 (2)	9844 (7)	16155 (2)	21935 (1)	6966 (4)	8343 (0.6)	9487 (13)
Mg	2201 (18)	2305 (2)	3694 (4)	4407 (2)	4439 (4)	5256 (1)	5627 (6)
Ca	25410 (29)	26985 (<1)	42195(<1)	44000	71795 (1)	99605 (3)	102760 (6)
Si	112 (<1)	-	152 (10)	362	715 (26)	983 (6.6)	952 (2)
Fe	230 (44)	280 (5)	624 (49)	868 (12)	603 (10)	1096 (3)	952 (2)

Arundo donax

	rhizomes			**culms**		
T, K	**703**	**753**	**873**	**703**	**753**	**873**
	mg/kg db					
Na	910.9 (<1)	1013.4 (25)	1803 (1)	556(10)	628 (6)	635 (4)
Al	2575 (2)	6479.5 (29)	9267.5 (4)	71 (12)	91 (25)	94 (5)
P	7018.5 (2)	8672.5 (13)	10009.5 (<1)	6590 (9)	7957 (8)	8514 (3)
K	28635 (1)	33140 (<1)	38900 (1)	16660 (11)	20257	20870
Mg	2202 (3)	2605 (21)	3291.5 (2)	1597 (10)	1985 (1)	2003 (1)
Ca	3601.5 (3)	4953 (25)	7321.5 (<1)	1434 (28)	1504 (1)	1482 (4)
Si	797.5 (<1)	-	-	-	596 (9)	492 (1)
Fe	1907 (2)	2374.5 (34)	3681.5 (<1)	97 (9)	106 (<1)	121 (6)

Table 8.1: ICP/MS analysis of the chars. SD is given in brackets.

The same approach adopted for data analysis of the PTEs also was conducted for K and P.
The species P and K were characterized by comparable trend, especially if they were part of the same feedstock.

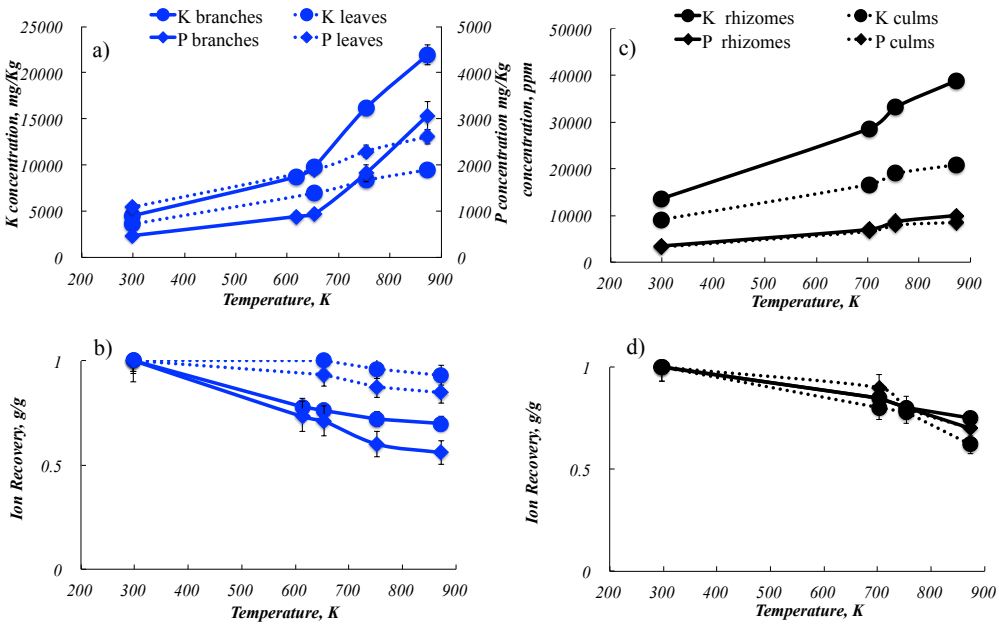

Figure 8.5: Concentration (a and c) and Ion Recovery (b and d) of Cu and Zn in the chars: P. nigra (leaves) and Zn in the chars from A. donax (rhizomes and culms) at different final temperatures.

Comparing the results of the chars produced at 873 K, the devolatilization of K was higher than the phosphorus one in the branches case. Whereas, in the sample of the leaves, the potassium were more stable. The K and P recovery in the chars was about 80%.
It was to notice that for the potassium contents in chars were always higher than phosphorus in the raw materials. For instance, in the branches the K content was 4477 mg/Kg and P was 468.4 mg/Kg. As could be expected, these values are characteristic of the lignocellulosic species, as mentioned in the chapter on the non-contaminated biomasses.
Also for A.donax was reported the K and P concentration and recovery in the chars. It should be noted that the same performance was observed for the two organs of A.donax. The K and P elements were characterized by the same behaviours even if were originated by different organs of the plant, contrary to the P.nigra. Observing the panel "c" is possible to notice that the concentration of K increases with the temperature more in the case of rizhomes, than in the

culms one. For both cases, the concentration of P increases in the same mode. The equivalent Ion Recovery, reported in panel "d" was comparable among all chars. At 873 K the 65 % of K and P recovery was obtained for the two parts of A.donax.

8.3 BET analysis

As shown in literature the solid product characteristics strongly depend on the feedstock, temperature and pyrolysis conditions. Slow steam assisted pyrolysis is a thermal treatment that provides chars with high value of specific surface area removing the volatile compounds and preserving the structural characteristics of the raw materials.
In order to investigate the potential applications of the char a comparative study on the physical characteristics of the contaminated chars obtained from the different parts of P. nigra and A. donax at different temperatures was conducted. The final pyrolysis temperature has a crucial role in determining the structural characteristics of the char. The influence of temperature and of the feedstock on the specific surface area of chars was shown in Figure 8.6.

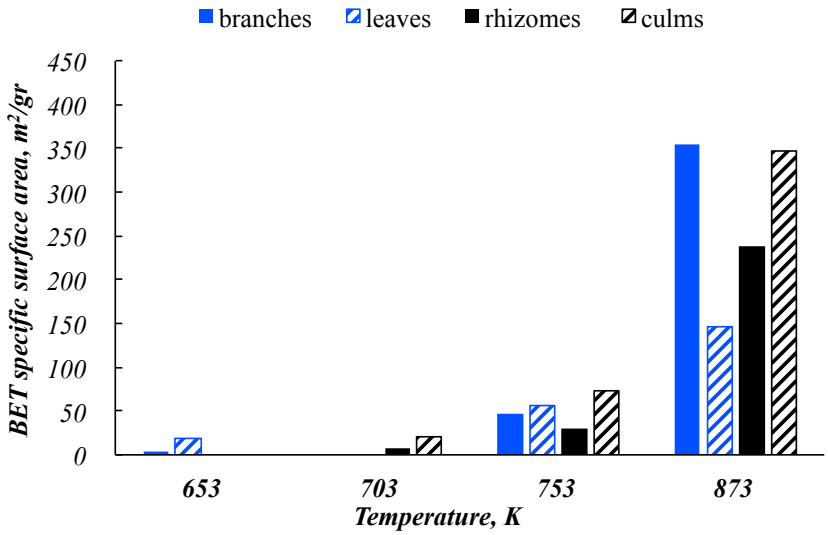

Figure 8.6: BET surface of the P. nigra (branches and leaves) and A. donax (rhizomes and culms) chars obtained from pyrolysis at different temperatures.

The BET values increased with the increasing of pyrolysis temperature. At 873 K, the formation of cracks in the material caused a great increase in surface area and porosity probably due to the development of micropores and mesopores (Lehmann et al., 2009). The comparison between the not contaminated biomasses and the different parts of the two contaminated biomasses allows to infer other insight on the effect of feedstock composition on the char porosity. Indeed, differently from Eucalyptus, the BET surface of char obtained from the different parts of Populus and Arundo increases with the temperature up to 873 K. At 753 K, the structure of the char was still compact for all the chars.

However, a trend can be observed even when the microporous region is not yet developed. At this temperature, the highest BET surface was obtained for Arundo culms, followed by the similar values obtained for Populus branches and leaves, and finally Arundo rhyzoms. At higher temperatures, the development of micropores enhances the differences between the different parts of the plants. At 873 K, the highest BET values were obtained for culms K namely 347.5 m^2/g and branches 325 m^2/g, followed by rhizoms and leaves (145 m^2/g). The development of the microporous region is due to the release of liquid tars produced and still entrapped in the solid matrix at lower temperature. On the basis of this consideration the highest values of BET surface obtained for branches and culms can be related to their highest content of volatiles that leave a greater portion of micropores in the solid matrix after their devolatilization. In fact, the content of volatiles in these two biomasses is similar, about 74 %, and it is higher than the volatiles content of rhizomes and leaves. Another reason for the low value of BET surface observed for leaves at 873 K, that is in contrast with the trend observed at 753 K, is the high content of ashes in this biomass (about 16%) that could determine the formation of fused intermediates at 873 K, responsible of occluding part of the porous structure of the carbonaceous matrix.

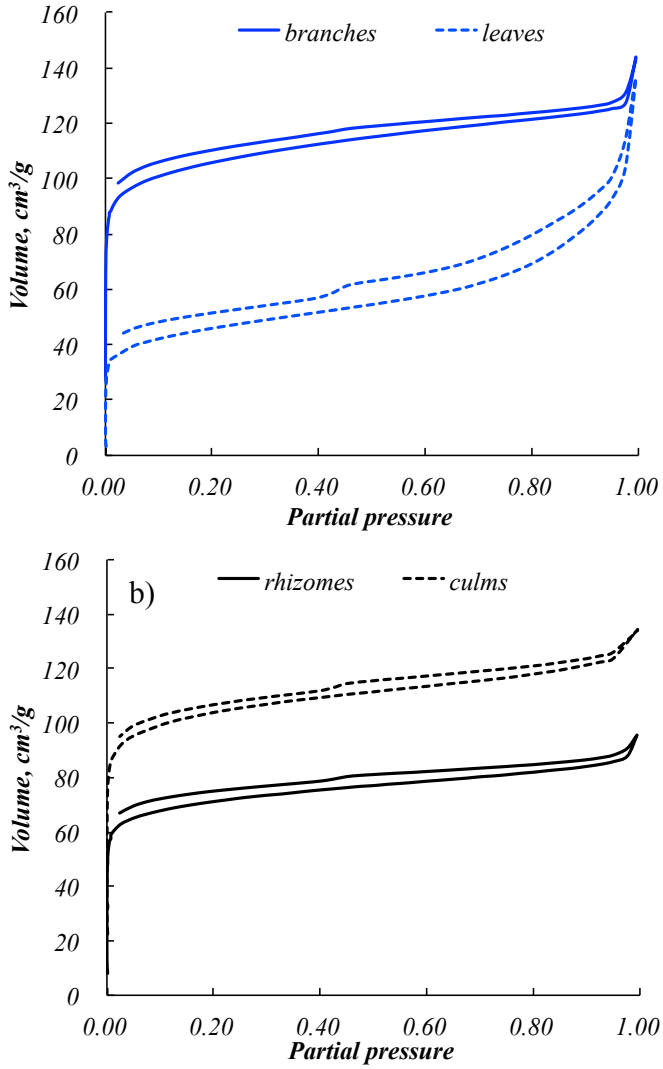

Figure 8.7: Adsorption isotherms of chars produced at T=873 K for Populus (a) and Arundo (b).

The morphology of chars obtained at 873 K was studied more deeply by adsorption tests.

All the isotherm curves, reported in the Figures 8.7 were "type II", according to with IUPAC classification (Sing et al., 1985) with H4 hysteresis. These Type II isotherms are associated with narrow slit pores including pores in the micropore region. The most striking feature of the argon isotherms is the presence of great ‘‘low-pressure hysteresis”, which is related to the entrapment of adsorbate molecules in very fine ultramicropores with dimensions close to those of the adsorbate (Bailey et al., 1971), thus making the pore size distribution analysis

difficult. Neverthless, the shape of the isotherms gives some indications of char morphology. The uptake of Argon in the low partial pressure region indicates the presence of a microporous region, more developed for culms and branches. This observation is in agreement with the trend observed for BET surface. In the medium partial pressure region, the argon uptake is limited for all the chars except for leaves. Moreover, for leaves char a steep increase of the argon uptake at partial pressure close to 1 is observed. These observation, suggest for this last char a higher extension of the mesoporous and macroporous region, in agreement with the lowest value of BET surface obtained for this char.
In the table 6.4 the total pore volume and the micropore and mesopore volume and area is reported for all the chars produced at 873 K. Branches and culms chars show similar values of the total pore volume, and of the microporous and mesoporous region in agreement with the similarities already observed between the adsorption/desorption isotherms and the values of BET surface. The microporous region prevails on the remaining porosity and determines the high value of the BET surface at 873 K. Rhizomes are characterized by a similar mesoporous region; on the contrary, the microporous fraction is less developed even though it gives the main contribution to the BET surface. Char from leaves has a completely different structure. It is characterized by a greater mesoporous fraction that accounts for the 66% of the total BET surface and and for the 92% of the total pore volume.

	Total pore volume	Mesopore		Micropore	
		MPV	MPA	MPV	MPA
	cc/gr	*cc/gr*	*m^2 /gr*	*cc/gr*	*m^2 /gr*
branches	0.16	0.05	56.47	0.11	297.72
leaves	0.13	0.12	100.29	0.01	45.62
rhizomes	0.11	0.05	53.01	0.06	185.19
culms	0.16	0.05	50.76	0.11	296.77

Table 8.2: Pore size distribution of the chars produced at 873 K (MPV: meso/micro pore volume; MPA: meso/micro pore area).

8.4 Heavy metals stability: leaching test on contaminated chars

The total heavy metal concentration in char is useful as an overall pollution indicator of the biomasses, but the environmental impact always depends on the leachability and bioavailability of metals within char. The safe application of the char has to be pursued; thereby the stability of PTEs was evaluated through extractions in different aqueous solutions. Three different solutions were used for the extractions, in order to simulate the potential using conditions of the char and to evaluate the bioavailable PTEs.
The "bioavailability" is the mobility of the PTEs from the char to the environment.
The extraction through water solution provided the information for easily extractable metals ions it means the soluble fractions. The ion-exchangeable fraction gives indications on the elements weakly adsorbed by means of electrostatic interactions released through ion exchange processes. It is determined using the $Ca(NO_3)_2$ solution.
Finally, the EDTA solution, buffered with acetic acid and ammonium acetate, was used in order to have information on the inorganics associated to the organic matrix
The NH_4-Ac-EDTA and the two buffer solutions represent the solubility of the organic part and carbonate-associated fraction.
Results of leachability tests are presented as the released amount of the specific ion with respect to the amount of the same ion in the original char.
The leachability of all the metals have been studied except for Cd since its content in chars was always close to the detection limits (1 mg kg^{-1}), thus affecting greatly the reliability of the obtained results.
In Figure 8.5 the leachability in the three solutions of the other metals from and from corresponding chars obtained at different temperatures was reported.

An interesting finding was that all the metals in the char were more strongly bound than in the original biomass. This is demonstrated by the release of all the metals in the H_2O extraction of the raw biomass. The higher release is observer in the order for Zn>Cd>Cu and Pb. For all the char, the release of water extractable metals is negligible except for a very low release of Zn, lower than 0.004%. Kloss et al. (2012) obtained a comparable result by for trend of the Cu and Ni. A possible reason for this result could be found in the alkaline environment induced by the char at increasing production temperature (see chapter 5, Tables 5.4 and 5.6) that does not allow the solubilisation of the metals salts in the alkaline aqueous solution.
The extraction of raw leaves in the $Ca(NO_3)_2$ and NH_4-Ac-EDTA solutions does not release any metals. A similar behaviour is observed for the extraction of all the chars in the $Ca(NO_3)_2$, whereas the release of metals from the chars

extracted with the NH_4-Ac-EDTA solution is observed only in the char produced at 873 K in the order of Pb>Zn>Cu. These results suggest that during the pyrolysis process the organically bound metals are retained in carbonaceous structures that undergo to chemical transformations during the process and become more bioavailable at higher pyrolysis temperatures.

The leachability of the metals in all the chars produced at 873 K from the different feedstocks has also been assessed and the results are presented in Figure 8.6. The metals concentration in the char from culms was very low, so it was not measured. As the water, extractable metals are below the detection limit the results obtained by the water extraction are not shown in the Figure. Moreover, as Cd is not retained in the chars obtained at 873 K, its concentration in all the extraction solutions has not been measured.

The extraction of chars in the $Ca(NO_3)_2$ solution determines the release of very low amounts of metals, mainly Pb and Zn. Zn seems to be the less stable except for the chars from rhyzome. However, the release of the metals in this solution is so low that the results could be affected by a significant error.

The release of metals from the chars extracted with the NH_4-Ac-EDTA solution is always lower than 0.1 except for the Pb from rhizomes char that is about 0.65 and account for about 80% of the Pb retained in the char. Pb is always the less stable followed by Zn and Cu. As NH_4-Ac-EDTA solution is able to destroy the organic matrix and the inorganic carbonates the retention of the metals after NH_4-Ac-EDTA extraction suggest the presence in the chars of very thermally stable inorganic compounds.

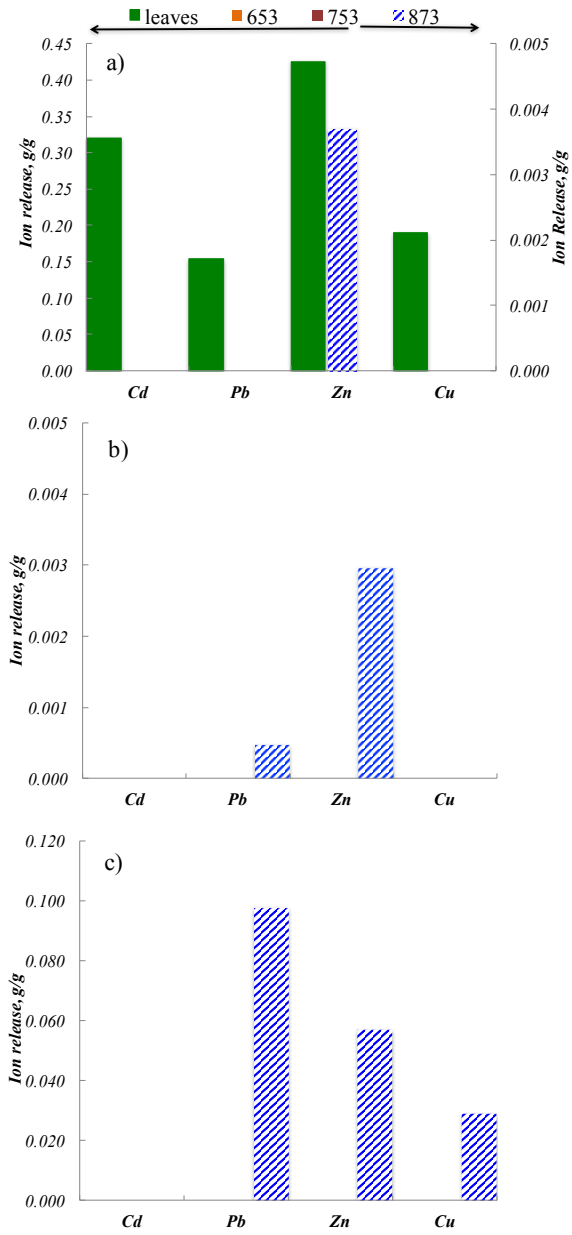

Figure 8.5: Metals leachability from leaves and corresponding chars extracted with water (a), $Ca(NO_3)_2$ (b) and NH_4-Ac-EDTA (c).

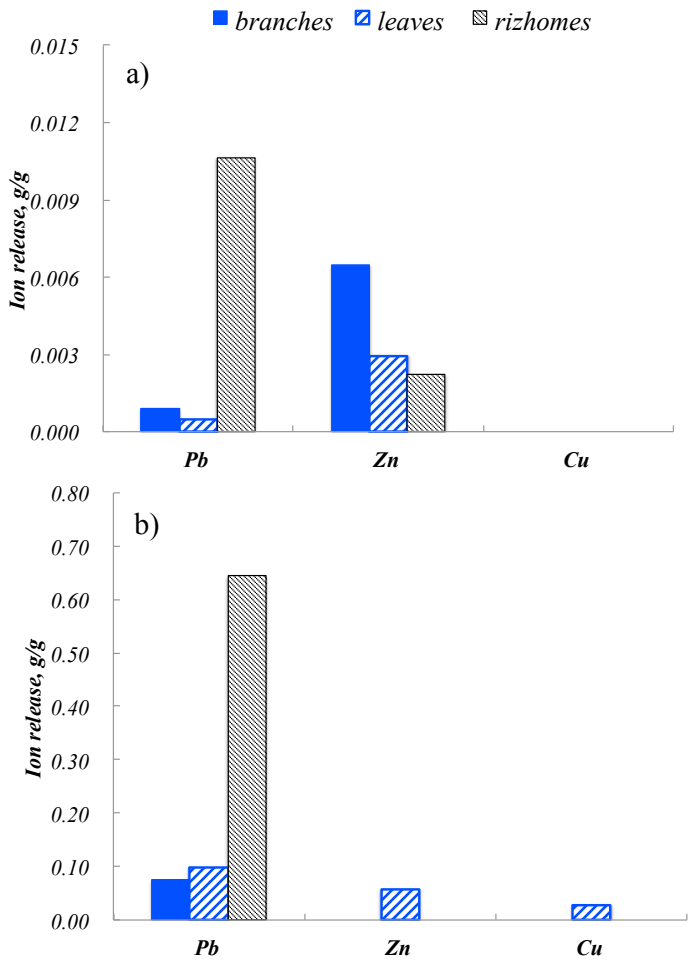

Figure 8.6: Metal leachability from all chars produced at 873 (a)Leached by $Ca(NO_3)_2$ – (b)by NH_4-Ac-EDTA

It would be expected that chars with the highest mesoporous and macroporous fraction can came more easily in contact with the extracting solution, but no correlation can be established between the release of the metals from the chars obtained from the different feedstocks and the meso and macro porosity of the chars. However, NH_4-Ac-EDTA solution is able to destroy the organic matrix and the inorganic carbonates. Consequently, the porosity of the material can be altered during the extraction and could be very different from the one of the original char.

9. Conclusion

In this work of thesis pyrolysis is studied as possible thermochemical treatment of the contaminated biomasses with the aim to:

- concentrate heavy metals in the solid product (char), thus reducing the volume and weight of contaminated matter.
- produce a combustible gaseous product containing no or limited amounts of heavy metals that can be used to assist energetically the pyrolysis process.
- tailor the characteristics of the char thus making it suitable for use in other applications.

The work is structured in two parts, in the first part the structural properties of not contaminated biomasses as function of the thermal conditions and feedstock chemistry are assessed, whereas in the second part the fate of the heavy metals during the pyrolysis of contaminated biomasses conducted in the same conditions has been studied.

The dependence of the properties of solid residue on the process final temperature was studied for Eucalyptys occidentalis Endl. in the temperature range of 688-967 K.

Tests on E. occidentalis char at increasing final temperatures show that:

- The fixed carbon content reached its maximum at 873 K, due to the onset of char oxidation reactions at higher temperatures.
- The HHV followed the same trend as fixed carbon content. Careful control of pyrolysis temperature was mandatory when steam-assisted pyrolysis was conducted with the aim of exploiting the char energy content. In this case, the management of ash was a problem, given the high concentration of inorganics in the char residue.
- The char surface becomes alkaline in nature at low temperature. Mild thermal treatment ($T < 794$ K) should be conducted if neutrality was desired.
- The char BET surface had a nonmonotonous trend with temperature; at 688 K, the char still had a compact structure, whereas the highest value occurred at 794 K.

Over 873 K, the high temperature affected negatively the development of the properties of the char. The best temperature range for the good char properties was: 794 - 873 K.

The comparative analysis between the chars derived from different feedstocks shows that the chemical nature of the biomass had a relevant role in the determination of char yield and properties as summarized in the following:

- Char yield depend on the content of lignin as well as of alkali and earth alkali metals. Under the pyrolysis conditions used in this work thesis, a linear correlation was observed between the yield of the organic fraction of char obtained at 873 K and the product between lignin content, cellulose content and the content of both alkali and earth alkali ions.
- All the produced chars, especially P. nigra char, had an O/C value lower than 0.2, revealing a high degree of aromaticity and maturation.
- All the chars were alkaline in nature, due to the presence of alkali and alkaline earth metal ions. In particular, the S. alba and F. oxyphylla chars had the highest content of exchangeable cations (Na, K, and Ca).
- The P. nigra and E. occidentalis chars exhibited the highest HHV, in agreement with the fixed carbon content and the lowest ash content. Moreover, the highest char yield was obtained for E. occidentalis determined its highest ER value in the corresponding char.
- Type II isotherms characterized all the chars and were associated with narrow slit pores including pores in the micropore region. The P. nigra and E. occidentalis chars seemed to be the most promising in terms of specific surface area.
- A correlation between the cellulose content in the feedstock and the development on the BET surface area was observed.

The results of the first part of this study reveal that E. occidentalis char is the most appealing to be tested for energy applications, P. nigra should be considered for carbon sequestration in soils and for use as a sorbent of undesired species in fluid stream and F. oxyphylla and S. alba could be applied in agronomic applications as nutrients source.

On the basis of these results, E. occidentalis, P. nigra were selected for the phytoremediation of polluted soils. A. donax was included within the phytoremediation test, due to its spontaneous growth in contaminated soils and easily harvesting. The behaviour of Pb, Cd, Cu and Zn during pyrolysis has been studied.

The effect of the variable feedstock (P. nigra and A. donax were resulted contaminated) and of the temperature, in the range 613-873 K, was studied

The results were showed that:

As the temperature of pyrolysis increases, devolatilization of all the heavy metals present in tested biomass increases. In particular, their recovery in solid phase remains constantly unitary as the temperature increases until it reaches a critical value, variable depending on the metal considered, above which the recovery of the metal in solid phase decreases with the temperature. The devolatilization of the Cd begins around 653 K and can be considered almost complete for a temperature of about 753 K. The release of Cd is very fast except for rhizomes where it proceeds more slowly. Due to the fast

devolatilization the concentration of Cd in the chars increases with the temperature up to 653 K than decreases at higher temperature. A different behaviour has been observed for Zn, Cu and Pb, whose devolatilization begins at 653 K, but it proceeds much more slowly. At 873 K about 80-85% of the metals are still immobilised in the solid phase. For this reason, the concentration of these metals in the chars continuously increases up to 873 K. Contrary to Cd, any relevant effect of the feedstock nature on the devolatilization of these metals has been observed.

- All the metals in the chars obtained at increasing temperature and from different feedstocks were more strongly bound than in the original biomass in H_2O solution. In all chars, the concentrations of water extractable and $Ca(NO_3)_2$ exchangeable metals were negligible.
- The mobility of Pb, Zn and Cu were observed only in the NH_4-Ac-EDTA solution and only for the char produced at 873 K, indicating that after pyrolysis these metals are retained in part bound to the organic matrix or in carbonates. This is particularly true for Pb in the rhizomes. In this case the 85% of the retained Pb is released in the NH_4-Ac-EDTA solution. For the other cases only the 10% of the retained metals is released in NH_4-Ac-EDTA solution.

The results obtained in this work of thesis show that when a slow pyrolysis process in has to be used for the treatment of the heavy metals contaminated biomasses the type of pollutants should be assessed. In presence of Cd it is necessary to operate at low temperature conditions (less than 553 K) to avoid the release of Cd into the combustible gaseous phase. However, under these conditions, the char characteristics do not allow to use it in processes that involve solid-fluid interface phenomena (e. g. adsorbing material, catalysis, synthesis of composite materials). The pyrolytic treatment in these cases represents only a safe biomass disposal process that combines the reduction of the volume of contaminated solid with an increase in its recalcitrance and a reduction of the mobility of heavy metal that remains confined in the char in a more stable form. If the biomasses are only contaminated with one or more metals between Pb, Cu and Zn, it is possible to conduct a pyrolytic treatment at higher temperatures, thus obtaining a solid residue of interest in all applications that require a high specific surface with retained metals present in more stable form hardly bioavailable, except for specific cases as was the case of Arundo rhizomes.

10.Suggestions for future work

Further investigations are required to understand the fate and transformation mechanisms of PTEs in the char production process.

The unresolved issues concern the different devolatilization behaviour observed for Cd on one side and Pb, Zn and Cu on the other side. The first one is very devolatilizes completely in a very narrow temperature range except in Arundo Rhizomes, whereas the devolatilization of the second group of elements occurs very slowly. This suggests that Cd is mainly present in a unique chemical forms, probably inorganic, except in rhizomes, whereas the metals of the second group could be linked to the ligninic matrix that devolatilizes slowly in a wide temperature range. Future work is needed to clarify this aspect.

Moreover, even if the tests were carried out in pyrolysis conditions, the steam probably affected the chemical reactions to which the inorganic elements undergo. The influence of the carrier gas on the PTEs devolatilization is another important point to be investigated.

As for the leaching behaviour the different behaviour of Pb in char obtained from rhizomes at 873 K should be investigated in more detail. It is almost completely released in the EDTA solution. On the contrary, in the same solution Pb retained in the chars obtained at the same temperature from the other is more stable and no more than 10% is released.

Finally, a detailed analysis of the surface chemistry of the chars could provide useful indications on future chars application.

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